

problem, it would be necessary, either to obtain an exact knowledge of the impurities in the water, so as to allow for their effect, or to use water which contained no such impurities. In the water distilled in air it is probable that ammonia and carbonic acid are dissolved ; if so, the effect in diminishing the conductivity necessarily follows.

Studies of the Processes operative in Solutions.—Parts VI—X.

By Professor H. E. ARMSTRONG, F.R.S. and others.

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Authors' title slips :—C D VI—X.

- VI D 7050 Title.
- D 7175 Nature of the process of dissolution.
- D 7275 } Explanation of electrolytic conductivity.
- C 6250 }
- D 7090 (Hydrolysis) Title.
- D 7090 (Neutralisation) Interaction of acids and alkalies explained on association hypothesis.
- D 7260 The ionic association hypothesis.
- D 7170 Viscosity, explanation of.
- D 7300 Optical properties and the association hypothesis.
- VII D 7065 Title.
- D 7090 (Hydrolysis) Title.
- D 7275 Title.
- VIII D 7090 (Hydrolysis) Title.
- D 7190 Degree of hydration of salts in solution.
- IX D 7315 Title.
- D 0910 } Polarimeter appliances.
- C 4000 }
- X D 1820 Title.
- D 7275 Title.
- D 7315 Title.

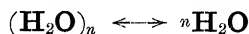
VI.* *Hydrolysis, Hydrolation and Hydronation as Determinants of the Properties of Aqueous Solutions.* By H. E. ARMSTRONG, F.R.S.

In this communication I desire to take a definite step towards an explanation of the fundamental changes attending dissolution and other operations in

* No. I, 'Roy. Soc. Proc.,' A, vol. 78, 1906, pp. 272—295 ; II—V, 'Roy. Soc. Proc.,' A, vol. 79, 1907, pp. 564—597.

aqueous solutions, by contending that dissolution involves associative and distributive changes which are necessary precursors of all chemical interchanges effected in such solutions.*

Both in my address to the Chemical Section of the British Association in 1885 and in my communication to this Society in 1886,† stress was laid on the reciprocal parts which solvent and solute play in the process of electrolysis. But I went too far in attributing, in all cases, the increase in molecular conductivity which is usually conditioned by dilution to the gradual molecular simplification (depolymerisation) of the dissolved substance. Moreover, although I contended that water plays a dominant part and called attention specially to its complex molecular structure, I but dimly perceived how great must be the influence exercised by the change effected in the composition of water itself—and the consequent alteration in its properties—when a substance is dissolved in it; the nature and *all-important* character of this influence only became apparent to me after the discussion on ionisation in Section A at the British Association at Bradford in 1900.‡ The consequences of the assumption that the dissociative change pictured in the equation



is of constant occurrence in water were somewhat more fully developed in my communication to this Society “On the Origin of Osmotic Effects.”

Nature of the Process of Dissolution.—Although in the case of salts and not a few other substances the simplification of polymers undoubtedly plays an important part, judging from its volatility it is probable that a substance such as hydrogen chloride enters into solution in water entirely in the monadic form, as HCl: in any case, it is unlikely that molecular complexes are ever present, even in the most concentrated solutions of this hydride, in proportions sufficient to account for the considerable changes which attend the dilution of such solutions. Hydrogen fluoride and sulphuric acid, on the other hand, both exist, presumably, to some extent in the form of polymers, even in moderately dilute solutions.

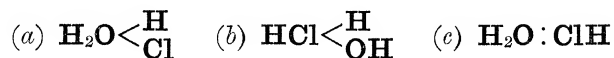
A satisfactory and, I believe, complete explanation of the properties of solutions of hydrogen chloride may be given on the assumption that when it

* Since 1885 my conviction has never varied that the hypothesis that the ions are free in solutions is one which does not and cannot afford an explanation of the facts as these present themselves to the chemist. It is only because chemical considerations have been laid aside and because the problem has been regarded from an artificial standpoint that the hypothesis has met with acceptance.

† ‘B.A. Report,’ 1885, p. 952; ‘Roy. Soc. Proc.,’ vol. 40, p. 268.

‡ ‘Encyclopædia Britannica,’ 1902, vol. 26, p. 741.

is dissolved in water interactions take place which involve the production of the following complexes:—



Definite expression is here given to the manner in which the “residual affinity” of the negative elements is exercised on which I laid much stress in 1885 and 1886, at a time when chemists were in no way prepared to acknowledge the extent to which this force is operative in conditioning chemical change.

I regard the bipartite, composite molecules (a) and (b) as the effective molecules and propose to speak of such complex molecules as the effective molecules and of their active components as the effective radicles in a solution of hydrogen chloride; being closed systems, molecules of the type $\text{H}_2\text{O} : \text{ClH}$ are inactive so long as they remain unmodified.

I avoid the terms ion, ionised and ionisation advisedly, as these now have an ambiguous meaning.

In the process pictured, the dissolved substance is in part hydrolysed, the component radicles being rearranged—*but not set free*; at the same time, the simple molecules contained in water also undergo scission and their component radicles are, in like manner, rearranged—*but not set free*. *I regard this double effect of admixture as a necessary step in the formation of a composite electrolyte.*

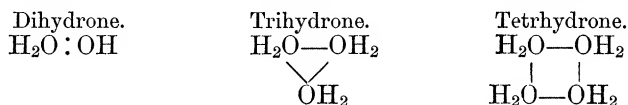
In cases in which only the molecules of the solvent undergo resolution, the solution obtained is not an electrolyte; in other words, composite hydrols of the type $\text{RX} < \begin{smallmatrix} \text{H} \\ \text{OH} \end{smallmatrix}$ when alone are not electrolytes.

This explanation of the process of dissolution is, I venture to think, generally applicable.

To consider the changes somewhat more in detail. Water itself, it is to be supposed, is a complex mixture of active and inactive molecules;* the active molecules being either simple monad-*hydrone* (OH_2) molecules or *hydrone-hydrol* (briefly, *hydronol*) molecules ($\text{H}_2\text{O} < \begin{smallmatrix} \text{H} \\ \text{OH} \end{smallmatrix}$); the inactive, the closed

* *Nomenclature*.—In order that a proper distinction may be made between the molecules in water which are to be regarded as active and the admixture of these with various inactive polymers which constitutes liquid water, I propose to confine the term *Water* to the admixture. It is inadvisable, I think, to follow Sutherland in speaking of the simple molecule of water as Hydrol, especially as this term was applied by me in 1880 to the unstable hydroxy-derivatives formed by the combination of the elements of water with aldehydes and acids (aldehydrols and acidhydrols). The *ol* terminal is now used strictly by chemists, as significant of the alcoholic function. Water belongs rather to the ketonic class—to the *ones*: the simple molecule H_2O may therefore be termed *Hydrone*; the term Hydrol may be reserved for use in reference to compounds in which the constituent radicles of hydrone function separately.

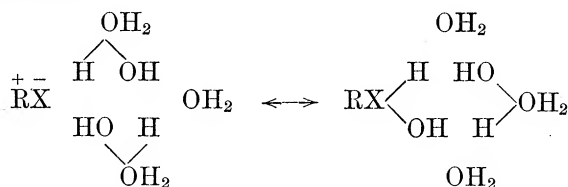
systems which are formed by the *association* unaccompanied by *distribution* of two or more simple molecules—such as are represented by the formulæ:—



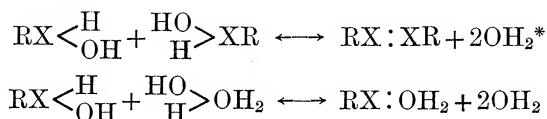
Whether or no all these modifications would arise in the entire absence of other substances is uncertain. Bearing in mind that it is possible both to super-cool and super-heat water in the absence of appropriate equilibrators, it is difficult to say what the behaviour of *pure* water would be: such a substance is and must ever remain an abstraction; under all ordinary conditions there must always be more than sufficient impurity present to determine the interaction of the various molecules.

Regarding the problem from the standpoint of Faraday's electrolytic studies, and in view of the well-known observations of De la Rive, Brereton Baker, Cowper and Dixon, I assume, however, that no two molecules can interact directly: that in all cases of chemical interchange (including electrolysis) the necessary *slope of potential* can only be provided by the inclusion of the interacting substances in a triple or tripartite conducting system.

It is probable that when non-electrolytes are dissolved in water they become modified in two ways. The primary change is determined, I assume by the hydrol molecules present in the liquid, the necessary slope of potential being provided, it may be supposed, by the interposition of an active hydrone molecule in the circuit.



The solution thus obtained is not an electrolyte, but contains the active complex $\text{RX} \begin{array}{c} \text{H} \\ \diagdown \quad \diagup \\ \text{OH} \end{array}$, the activity of which is conditioned by the *distributed* hydrol. Polymerides of the compound RX are formed by the interaction of these complexes; and they may be converted by the agency of hydrol into inactive isomerides in which the hydrone is associated with the compound RX,* but not distributed.



* In this and subsequent equations no attempt is made to indicate the nature of the "circuit" or system within which the interchange occurs.

In the case of substances which give rise to composite electrolytes when dissolved in water, I assume that not only is the compound hydrolated, but that its simple molecules also undergo distribution, so that the solution contains the isodynamic active complexes represented by the formulæ :—



It is to be supposed that the occurrence of electrolysis in such solutions is dependent on influences which the composite molecules exercise reciprocally upon one another whilst under the influence of the electric strain.

Electrolytic Conductivity.—The apparent increase in the electrolytic activity of a dissolved substance on dilution is presumably due to an increase in the proportion of effective composite molecules. Such increase is ascribable to the diminution in the activity of the solvent water which is conditioned by the increase in its relative amount. Water, in fact, must be regarded as most active when present in smallest amount, as it is then present mainly in the monadic form or in association *as hydrol*, change taking place more and more completely in the direction $(OH_2)_n \rightarrow nOH_2$ the greater the admixture of foreign substance. The withdrawal of hydrol from the effective composite molecules through the agency of the hydrol in the solvent water will therefore tend to a minimum when the solution is diluted, as the proportion of monads and of hydronol in the water becomes less and less.

In a solution of hydrogen chloride, for example, the existence of molecules of the type $HCl < \begin{smallmatrix} OH \\ H \end{smallmatrix}$ should be favoured in weaker solutions, as in these the solvent water will have less tendency to withdraw hydrol from the complex; on the other hand, in concentrated solutions, the proportion of effective molecules of the type $H_2O < \begin{smallmatrix} Cl \\ H \end{smallmatrix}$ should be larger than in weak solutions, as the hydrol should have greater hydrolysing efficiency in such solutions.

From this argument it follows that conductivity in concentrated solutions is conditioned mainly by molecules of the *hydrolysed* solute of the type $H_2O < \begin{smallmatrix} H \\ Cl \end{smallmatrix}$, whilst in weak solutions it is conditioned mainly by molecules of the *hydrolated* solute, *e.g.*, $HCl < \begin{smallmatrix} H \\ OH \end{smallmatrix}$; in other words, the solute is mainly active as hydrolyte in concentrated solutions, the solvent in weak solutions; and their respective molecular conductivity values must lie at opposite ends of the scale of concentration—supposing, that is to say, that it be possible to distinguish their separate effects.

The conventional conception of molecular conductivity, in fact, appears to

be based on a misconception;* and the same may be said of so-called ionic velocities. Hitherto only the negative ion derived from the solute has been taken into account, but that derived from the water present as hydrol must also be considered; when this is done and the sum of the two effects is allowed for, it will doubtless be found necessary to abandon the conception that the opposite ions of an electrolyte move at different rates. The conductivity values at extremely low dilutions are presumably in the main "hydrol" values; the reason why dilute solutions are so regular in their behaviour, however tested, is probably because in such cases the behaviour of the hydrol almost alone comes under consideration.

In discussing the problem of electrolysis in 1885 I drew attention to the current belief that when aqueous solutions are submitted to electrolysis the dissolved substance, not the water, is the actual electrolyte. It appears at least doubtful, I then said, whether this view can be justified by reference to known facts; and, after speaking of the special case of sulphuric acid, I added, "are not perhaps both (the acid and the water) affected according to the proportions in which they are present? The marked variation in the extent to which the negative ion is transferred to the positive pole, as observed by Hittorf, when solutions of different degrees of concentration are electrolysed would appear to support this view. The difference in the products, according as dilute or very concentrated solutions of sulphuric acid are used, may also be cited as an argument that the chemical changes vary with the concentration." I further pointed out that, in the event of such a view prevailing, it would be necessary to teach that the changes involved in the interaction of metals and acids were no less complex.†

In the meantime, McLeod's observations (1886)‡ on the electrolysis of solutions of sulphuric acid of different degrees of concentration and those of Haber and Grinberg§ (1898) on solutions of chlorhydric acid have shown that great differences are conditioned by concentration—differences which cannot well be explained except on the assumption that the acid system is

* Being a value deduced by merely multiplying the specific conductivity of a solution by the volume containing a gramme-molecular proportion of the solute, it is in no way necessarily to be associated with the dissolved substance alone. The "molecular conductivities" in a series of solutions are nothing more, in fact, than a series of numbers relating to solutions of comparable equivalent strength, expressing their relative specific activities as conductors.

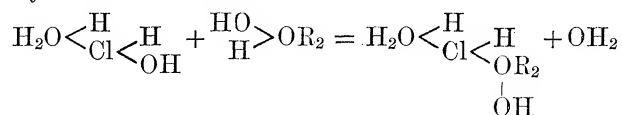
† Doumer has recently brought forward as novel this interpretation of the phenomena of electrolysis in the case of solutions of chlorhydric acid ('Comptes rendus,' 1908, vol. 146, p. 329; see also later papers).

‡ 'Chem. Soc. Trans.,' vol. 49, p. 591.

§ 'Zeits. anorg. Chem.,' 1898, vol. 16, pp. 198, 329.

mainly electrolysed in concentrated solutions and the isodynamic hydrolated system in weak—electrolysis being dependent in both cases on some reciprocal interaction of the two substances.

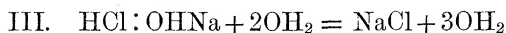
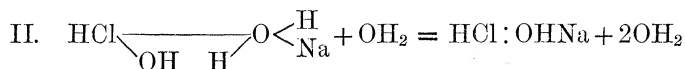
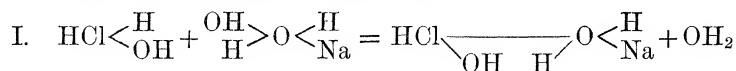
Hydrolysis.—Inasmuch as hydrolysis takes place the more readily the more concentrated the solution, it is to be supposed that it is conditioned by molecules of the hydrone type, $\text{H}_2\text{O} < \begin{smallmatrix} \text{H} \\ \text{X} \end{smallmatrix}$, not by the isomeric hydrolated complexes; moreover, that the hydrone enters into combination with the hydrolyte through the agency of the radicle X. Probably the hydrone is present in a hydrolated state, thus



Such a compound would be eminently unstable and readily break down in presence of hydrol—or in concentrated solutions under the influence of the isodynamic composites.

The behaviour of concentrated solutions of chlorhydric acid, to which reference is made in the next communication (p. 101), is in accordance with this interpretation of the character of the change.

Interaction of Acids and Alkalies.—The process of neutralisation may be supposed to take place in several stages, thus:—



The proportion of hydrol actually set free and the amount of water formed (I and II) will depend on the amount of associated hydrol in the effective composite molecules of acid and alkali, together with the molecular proportion liberated in the final change (III), less the amount effectively associated with the dissolved salt—at most, two molecular proportions, therefore. Inasmuch as hydrolation appears never to be complete (except sometimes in very dilute solutions) and is very far from being complete under all conditions in the case of weak acids and compounds such as ammonia, it is probable that the amount liberated, as a rule, falls considerably below two molecular proportions.

Ostwald, who has used the change in volume which attends the neutralisation of acids as a means of grading them in order of their relative affinities,

has already pointed out that the volume increase is greater than the volume of the water formed (in the final change marked III above). Thus, on mixing "kilogramme normal" solutions of nitric acid and potassic hydroxide, he observed an expansion amounting to 20.05 c.c.; but in the case of ammonia and nitric acid there was a contraction of 6.44 c.c., whilst on mixing acetic acid and ammonia the contraction amounted to as much as 16.26 c.c.

The method adopted by Ostwald of comparing solutions containing equivalent proportions of the solute *per kilogramme* is a peculiar one; when solutions are contrasted (Table I) containing comparable proportions of solute and solvent (weight-normal molecular), the results are more striking, differences becoming apparent which are not shown in Ostwald's table; thus the change in volume is considerably greater in the case of caustic soda than of potash, for example; no such difference was observed by Ostwald. It would seem that the hydroxide of sodium is more active than that of potassium, just as the sodium salts generally are more active than those of potassium.

Table I.

Vol. of weight-normal molecular solutions at 25°	KOH = 1014.68	HCl = 1021.98	
	NaOH = 1001.28	HNO ₃ = 1033.25	
Water, 1000 grammes = 1002.97 c.c.			
(KOH) + (HCl) = 2036.66 - 2005.94 = 30.72 c.c.			
KCl = 1031.92 + H ₂ O = 1049.97 - 1002.97 = 47.00 c.c.			Ostwald.
(18.05 c.c.)	Expansion = 16.28 c.c.	19.52	
NaOH + HCl = 2023.26 - 2005.94 = 17.32 c.c.			
NaCl = 1021.61 + H ₂ O = 1039.66 - 1002.97 = 36.69 c.c.			
	Expansion = 19.37 c.c.	20.05	
KOH + HNO ₃ = 2047.93 - 2005.94 = 41.99 c.c.			
KNO ₃ = 1043.48 + H ₂ O = 1061.53 - 1002.97 = 58.56 c.c.			
	Expansion = 16.57 c.c.	19.24	
NaOH + HNO ₃ = 2034.53 - 2005.94 = 28.59 c.c.			
NaNO ₃ = 1033.22 + H ₂ O = 1051.27 - 1002.97 = 48.30 c.c.			
	Expansion = 19.71 c.c.	19.77	

The difficulty of explaining such results from an ionic standpoint has never been sufficiently considered. On the assumption that when binary compounds which afford conducting solutions are dissolved in water they undergo dissociation into separate free ions, these latter must occupy less space than the substances from which they are derived, since the dissolution of such substances involves a considerable diminution in volume. But, according to this hypothesis, the neutralisation of an acid by a hydroxide merely involves the union of hydrogen ions from the acid with hydroxyl ions from the alkali, the other ions remaining unchanged—the expansion must therefore be entirely a consequence of this formation of water from free

hydrogen and free hydroxyl ions. These conclusions are scarcely such that they can be regarded as acceptable, as the increase in volume is largely in excess of the amount to be expected in the case of the stronger acids.

If, however, it be assumed that the change in volume on neutralisation is the measure of the difference between the water formed in the three ways shown above and that fixed by the resulting salt (including the changes in the state of dissociation of the water), a simple explanation is obtained applicable to ammonium salts as well as to metallic salts generally, the contraction in the case of ammonium salts being due to the fixation of the water by the salt, the amount fixed being very large in a case such as that of acetic acid in proportion to that liberated from the ammonia and the acid.

The precise character of the changes in volume which attend the dissolution of salts cannot well be determined, no means of estimating the liquid volume of the salt in solution being at our disposal. There is reason to believe that loosely held "water of hydration" has much the same volume as ordinary water. As ice has a volume so very different from that of liquid water, it is clear, however, that volume is a more or less relative matter; and if ice can exist of density 1.1, as stated by Tamman, some forms of water molecules are certainly capable of occupying considerably less space than we are in the habit of supposing.

The behaviour of non-electrolytes with water is also significant. To take the case of methylic acetate, as this is considered in the next communication, when the half of one gramme-molecular proportion (42.04 c.c.) is added to 1000 grammes of water at 25°, the volume diminishes by 5.67 c.c. or 13.5 per cent. It is scarcely probable either that the volume of the acetate changes materially on dissolution or that the acetate becomes hydrolated to any extent; consequently, the change in volume must be attributed, at all events in large measure, to an alteration in the water—to an increase in the proportion of hydrone and hydronol; and if this be the origin of the change, it follows that the volume of hydrone and of hydronol is less than that of water. In favour of this conclusion also we have the fact that the rotatory power of cane-sugar in solution is diminished in the direction of concentration by pressure (*cp.* I, p. 278) and that pressure diminishes the rate at which cane-sugar is hydrolysed (Röntgen, etc.); according to the view now advocated, the degree of hydrolation and hydronation of a substance such as sugar would be diminished by an increase of hydrol and hydrone and pressure should favour the dissociation of water into hydrol and hydrone if the latter have the smaller volume.

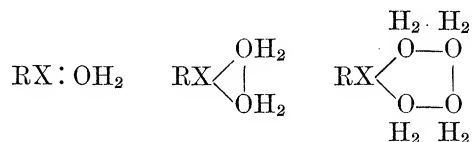
Moreover, applying considerations such as have been developed by Barlow and Pope, there is reason to suppose that considerable condensation, if not

a complete disappearance, of their volume might attend the fixation of hydrone as hydrol in the manner pictured, especially as this involves the close packing of the radicles H and OH, not of the actual hydrone molecules in the assemblage.

According to these assumptions, the changes of volume which attend dissolution, and especially those which attend dilution, apart from those arising from changes in the water, are largely, when not entirely, a consequence of constitutive changes—being mainly conditioned by the degree of effective hydration—*i.e.*, hydrolation, etc., of the molecules of the solute. As there is reason to suppose, however, that salts are only gradually resolved by dilution into the monadic form, the change in volume is not in itself a simple measure of the extent to which the molecules are rendered effective by hydrolation; the slowness with which hydrogen fluoride, for example, increases in conductivity would seem to be sufficient proof that the depolymerisation process may be a very gradual one even in the case of a volatile substance.

In concentrated solutions, active molecules of the solute presumably exercise an effect comparable with that which active molecules of the solvent produce in less concentrated and dilute solutions: in fact, the two series of effects must be regarded as operative throughout the entire range of concentrations.

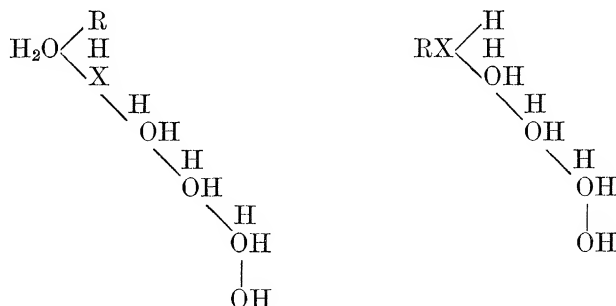
Hydration.—At present no very definite conception is attached to the term hydration. From the point of view advocated in this communication, the process may be of two kinds, according as it involves either hydrolation or hydronation. It is assumed that the primary product is a simple hydrol; this may undergo change in two ways and give rise either to a simple or a compound hydrone or to a poly-hydrol. In the former case, compounds such as the following are produced:—



It cannot be supposed that the number of molecules which can be associated in closed hydrone chains is unlimited—probably, as in the case of carbon compounds, a superior limit is soon reached. Hydrone, in this state of combination, is to be regarded as withdrawn from the sphere of action and as exercising a screening effect on the molecule with which it is associated.

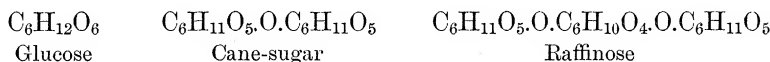
In the case of composite electrolytes, on the other hand, the molecules of the solute may be thought of as hydrated in a way which does not deprive

them of their activity but, on the contrary, enables them to exert their influence at a distance—thus :



The length of such chains would depend on the character of the competition within the solution. Such chains are possibly the conveyors of the current in a liquid electrolyte—they must be thought of as constantly subject to attack from outside by other hydrolated molecules: therefore, as being constantly broken down but remade as constantly.

Reference is made in the following communications (VIII, p. 108 ; X, p. 130) to the remarkable manner in which the three sugars



reduce the conductivity of salts in solution—practically in proportion to the number of oxygen atoms which they contain. It is therefore probable that each oxygen atom becomes hydrolated (if not polyhydrolated) and that the great influence exerted by the sugars in solution is the consequence of the association of hydrol in this manner with their molecules; as a result, they not only become powerful dehydrolating agents and by their action on hydrolated salt molecules reduce these latter to an inert condition, but are also eminently attractive of the hydrol and hydrone in water and consequently influence the osmotic properties generally of the solution.

It should be pointed out that in presence of hydrolated compounds the equilibrium conditions in the water present in the solution will be disturbed and therefore different from those in ordinary water. Consequently, it is to be expected that the proportions in which the two constituents of a composite electrolyte are present in a simple solution will be altered when another substance is introduced into the solution which modifies the composition of the water—and that no amount of dilution will quite restore the equilibrium. The behaviour of mixtures of electrolytes and of mixtures of electrolytes with non-electrolytes is apparently such as to be expected from this point of view.

Ionic Properties.—Whether the distribution of affinity in such chains as are referred to above be equal throughout or at a maximum at their origin is uncertain. The degree of affinity with which hydrol and hydrone are held in the molecule must depend on the nature of the compound RX and will vary according to the influence exerted by R upon the negative radicle X —according as X is more or less neutralised by R . Hence also the difference in the conductivity values of different electrolytes. I doubt whether the conception of a constant atomic charge introduced by Helmholtz be defensible from the point of view advocated in this communication. It has recently been admitted by Larmor, in his Wilde lecture, that the structural conceptions of chemists are to be regarded as having something more than a mere symbolic meaning. If we accept the geometric conceptions introduced by Barlow and Pope—which undoubtedly are of the first importance as correlating structure with crystalline form and as affording a means of expressing relationships which have hitherto eluded treatment—we must suppose that volume plays a determining part and it may well be that Faraday's law will find a simple interpretation in volume considerations—that the relation of equality observed among electrolytes is the outcome of an equality in the number of volume units dealt with, just as when water is forced through a series of connected tubes differing in diameter the amount displaced in unit time is regulated entirely by the amount forced through the tube of least diameter.

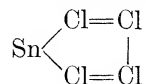
I have already put forward the contention that the conductivity of a binary solution cannot be ascribed to one of the substances only and that the current conception of molecular conductivity is a misconception. The opinion seems to be generally held that conductivity is a direct measure of the extent to which the molecules of the electrolyte share in the process of electrolysis—that the proportion of molecules active in two equivalent solutions may be deduced directly from their molecular conductivities. Such a conclusion is at least open to question—to take an example, that of hydrogen fluoride. It is supposed that few only of the molecules of this hydride are active in solution (dissociated) in comparison with the number active in an equivalent solution of hydrogen chloride, partly because the fluoride is present to a considerable extent in the form of associated molecules and partly because it resists dissociation more than the chloride does. It is far more probable that, owing to the intense affinity of hydrogen for fluorine, but a small proportion of composite molecules ($H_2O \text{ < } \overset{H}{F}$) in which the hydride is distributed, is formed in the solution; moreover, that the elements of hydrol are held so firmly in the hydrolated

molecules $\text{HF} < \begin{smallmatrix} \text{H} \\ \text{OH} \end{smallmatrix}$ that they are far less readily electrolysed than are the corresponding hydrolated hydrogen chloride molecules.

Again, the caustic alkalis have only about half the molecular conductivity of the strong acids. This might be supposed to be due to the presence in solution of a large proportion of associated molecules of the alkali; but a hydroxide such as tetramethylammonium hydroxide has practically no greater conductivity than potash or soda, and yet it is probable that it would exist in solution in an associated form to a far less extent than either of these. It appears probable that the elements of hydrol are held far more firmly by the alkalis than by even the strongest acids.

Electrolytes and Non-electrolytes.—Carbon compounds occupy a pre-eminent position as non-electrolytes. This is accounted for without difficulty as a consequence of the fact that when its four units of affinity are satisfied carbon does not manifest any appreciable degree of residual affinity; moreover, its influence over other elements, especially oxygen and chlorine, is altogether remarkable. In other words, carbon compounds are not electrolytes because only those negative elements give rise to electrolytes which assume more than one valency.

To account for the difference met with in the case of a number of metals between the lower and higher chlorides, for example, it is probably necessary to admit more or less profound structural differences and changes in the distribution of affinity consequent on the presence of an excess of chlorine. It is at least doubtful whether any metal have more than one valency—the manifestation of residual affinity is not improbably a non-metallic property. From this point of view, a compound such as stannic chloride—a non-electrolyte—may be represented by the formula:



The difference between it and the lower chloride may be supposed to consist in the fact that the latter and other chlorides which are simple electrolytes in the liquid state resemble water in that they are capable of existing in several different molecular states: to an extent, in fact, which makes the formation of tripartite systems possible without the intervention of other substances.

Compressibility of Solutions.—Solutions are often to a very considerable extent less compressible than water; the dissolved substance must therefore, directly or indirectly, exercise an influence within the solution tending to cause its compression. This is the phenomenon discussed by Nernst and others under the designation electrostriction.

Apparently, solutions of acids are less compressible than those of salts; those of ammonium salts come next, following which come those of lithium, potassium and sodium; solutions of nitrates are somewhat more compressible than those of chlorides, those of sulphates considerably less compressible. Unfortunately, the data at disposal are not deduced from observations made under comparable conditions, as only volume-normal solutions have been examined; consequently, no strict deductions can be drawn from them; it is clear, however, that substances fall into much the same order when arranged inversely according to compressibility as they do when arranged according to conductivity and hydrolytic activity.

Hence it may be assumed that the compressibility is dependent mainly, if not entirely, on the number of molecules of the solute which are rendered active by hydrolation, viz., conversion into effective bipartite composite molecules of the type $RX < \overset{H}{\underset{OH}{\text{O}}}$, the compressibility being inversely proportional to the number of such molecules.

Other Properties.—It is probable that the peculiarities manifest in the case of aqueous solutions generally are often expressions of an aqueous thirst conditioned by the tendency of the hydrol molecules effectively associated with the molecules of the solute by the force of residual affinity to couple with their kind in the manner represented on p. 86. In the case of composite electrolytes this argument is applicable to the two isodynamic complexes in solution.

Thus, if the viscosities of solutions be contrasted, it is obvious on comparing the viscosities of acids with those of their sodium salts that the difference is small in the case of strong, and large in the case of weak acids. Regarding the manifestation of viscosity as in the main a process in which the bipartite composite molecules are torn asunder as similar molecules and the molecules of the solute are forced over their surfaces, solutions containing a small proportion of such molecules—those of weak acids—would obviously be slightly viscous in comparison with those from which, for example, a large number of hydrol molecules can be torn off and converted into ordinary water.

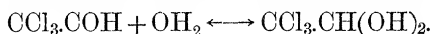
From the point of view here advocated, the depression of the freezing-point and of the vapour-pressure of water by salts—apart from the dissociation effect which these latter produce in the water—is attributable, in like manner, to the attractive influence exercised by the bipartite composite molecules aforesaid and to be proportional to their number.

Optical Properties.—The difference in the refraction equivalents of acids and their salts, which is small in the case of strong and large in the case of weak acids, is again attributable to the different influence exercised on

refractive power by the hydrol and hydrone associated with such compounds in solution, the difference being small in the case of strong acids, as the amount in association is more nearly the same in the case of acid and salt, whilst it is large in the case of weak acids, as only a small proportion of composite molecules are present in solutions of these acids, but a considerable proportion in solutions of their salts.

Perkin's observations on the magnetic rotatory powers of the acids and of their aqueous solutions, however, show clearly that discrimination must be exercised in explaining their peculiarities and that there are underlying complexities which need to be taken into account. In the case of the oxygenated acids, the change in rotatory power on adding small proportions of water is considerably less than is accounted for by the water itself, *i.e.*, the water enters into combination in a manner which involves a reduction in the magnetic rotatory power, but the extent to which this is the case diminishes as the dilution is increased. In the case of the halhydrides and other haloids, however, the molecular rotatory power of solutions is greater than the sum of the rotatory power of the anhydrous substance and of the water—the more so the greater the dilution.

In seeking for an explanation of these differences, it is necessary to take into account Perkin's observations on chloral and chloral hydrate, which show that the "water" fixed by the aldehyde has less than half the value of ordinary water. It is generally supposed that an aldehydrol is formed,



A similar explanation may be given of the change produced on adding small proportions of water to sulphuric and nitric acids. It is also not improbable that "hydrolation" should involve a diminution in rotatory power in the case of the halhydrides and haloids and of salts generally; the increase observed may be accounted for, however, if it be assumed that hydronates of the type $\text{RX}:\text{OH}_2$ are present in solution. Such compounds belong to the ethenoid or unsaturated class; compounds of this type, it is well known, exercise a greater optical effect than do saturated compounds. Hydrols, on the other hand, may be expected to have a relatively small effect.

One other use that may be made of the foregoing considerations remains to be mentioned, *viz.*, their application to the explanation of the effects produced at surfaces: such, for example, as Brownian movements, the evolution of heat on moistening powders, decoloration of solutions—including the withdrawal of dye stuffs by charcoal and other neutral materials—the flocculation of soils and Liebreich's "dead space" phenomena.

A plausible explanation of most if not of all of these effects may be given on the assumption that all surfaces in contact with water become more or less hydrolated and that in virtue of this condition they influence hydrolated molecules in the neighbouring liquid by withdrawing the elements of hydrol from them. From this point of view, the fact noted by Liebreich that, in dilute solutions of sulphurous and iodic acids, change first takes place in the axis of the tube in which the liquid is placed may be the consequence of partial dehydrolation of molecules in the neighbourhood of the surface of the tube and the consequent diminution in the number of potentially active molecules in passing from the axis of the solution to the periphery. The deposition of "dye stuffs" present in solution as loosely hydrolated "colloid" molecules may be accounted for in a similar manner—in fact, the explanation may be applied generally to the precipitation of colloids from solution by the addition of salts. The "inactive" region which, as Liebreich has shown, exists at the surface of an aqueous solution is probably one in which there is an excess of hydrol molecules—in which, consequently, hydrolated molecules become more depleted of hydrol than in the interior of the liquid, where there is an excess of water. The phenomena of surface tension may also be attributed to the preponderance of monads in the surface layer of a liquid.

The interpretation of the phenomena of chemical change and of electrolysis now put forward has the advantage that it involves the recognition of the essential unity of behaviour of the closely allied elements, oxygen and chlorine, for which I contended so strongly in the discussion at Leeds in 1890.*

But the conditions in solutions are represented as very complex and it will probably be more than difficult to evaluate the individual factors even in an approximate degree. One of the most essential steps to be taken is the determination of the condition of the water itself in a solution by direct measurement of vapour pressure, a task of no slight difficulty—to this end it is desirable to improve and simplify the method of determining vapour pressure at any desired temperature.

VII. *The Relative Efficiencies of Acids as deduced from their Conductivities and Hydrolytic Activities.* By H. E. ARMSTRONG and E. WHEELER.

It is commonly stated that nitric and chlorhydric acids are practically equivalent in strength and that sulphuric acid (contrasting molecular proportions) is somewhat stronger than either: the electrical conductivity

* 'B.A. Report,' 1890, p. 326; 'Zeits. phys. Chem.,' 1891, vol. 7, p. 418.

values on which this conclusion is based appear to have been determined in volume-normal solutions; in no case has the effect due to variation in such solutions in the amount of water displaced by the acid or of that apparently withdrawn by its hydration been taken into account. When the values deduced by R. J. Caldwell, using cane-sugar and gramme-molecular weight-normal solutions of chlorhydric acid,* are contrasted with those obtained by R. Whympers, using nitric acid, the difference is seen to be very considerable (the velocity constant at 25° being 504 in the one case, 465 in the other), far greater indeed than is observed in the case of the more dilute solutions.

Although—apart from the discrepancies conditioned by variations in the concentration—the conclusions based on other methods of contrasting the strength or affinities of acids appear to be broadly in agreement with those based on the determination of electrolytic conductivity or of hydrolytic activity, there is lack of evidence to what extent the differences are the expression of intrinsic peculiarities.

The method of contrasting the behaviour of substances in dilute solutions which has been so much in vogue of late years is obviously that which is most likely to render their specific properties inconspicuous and it is surprising that it has so long enjoyed popularity; it is even more surprising that, in the case of concentrated solutions, the practice should have so long prevailed of regarding absolute volume as of consequence and of disregarding altogether the great difference in the relative molecular proportion of agent and solvent which such a method of treatment often entails; had we ever given the subject consideration from a chemical standpoint, this remarkable oversight could never have been allowed in practice. For a similar reason the treatment sulphuric acid has received is altogether inconsiderate—that the acid which every chemist must recognise is far the strongest should have been allowed to pass as only of moderate strength (about two-thirds that of nitric acid) is clear proof that the critical faculty has been suppressed by the influence of authority and of fashion.

The experiments referred to in this communication have been made with a view of contrasting the behaviour of the three common acids—nitric, chlorhydric and sulphuric—as hydrolytic agents when associated with water in various proportions, in order to compare the estimates of their relative strengths thus arrived at with those deduced from the electric conductivities of the solutions, as well as in the hope of obtaining further evidence as to the exact nature of the processes of hydrolysis and electrolytic conduction.

Determination of Hydrolytic Activity.—The method adopted is that described in previous communications of this series. In determining the

* 'Roy. Soc. Proc.,' A, vol. 78, p. 287.

activity of 1/10 and 1/20 normal acids, however, the inversion was usually observed during its later stage. The temperature in the polarimeter tube having been adjusted at 25° and a reading taken, the tube was set aside at 25° until about 12 hours afterwards, when the next reading was taken; subsequently, observations were made every hour. The small errors in the readings during the later stages, when the change is slow, affect the value of the constant less than the larger errors which necessarily attend observations made during the earlier stages, when the extent to which change takes place is much greater. The majority of the observations were made in mercury green light.

The results recorded in Table I are those obtained by using a gramme-molecular proportion of each agent together with one-half of a gramme-molecular proportion of cane-sugar and 1000 grammes of water (or $1000/18 = 55.5$ molecular proportions).

Table I.

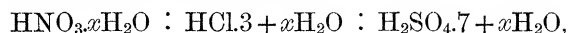
	I.	II.	III.	IV.	Mean.
$\text{HNO}_3 + 55.5\text{OH}_2$	466	469	468	469	468
$\text{HCl} + 55.5\text{OH}_2$	500	499	499	499	499
$\text{H}_2\text{SO}_4 + 55.5\text{OH}_2$	551	554	552	552	552

The rates of change observed in the case of the three acids are very different and it is obvious that equally concentrated solutions, *i.e.* solutions which contain equivalent proportions of the anhydrous substances—are not equally active. Bearing in mind the fact that the three compounds undergo hydration to different extents and also the argument developed in Part I of these Studies and in the Communication on the Nature of Osmotic Effects by one of us, it is clear that solutions containing equivalent proportions cannot be of equivalent strength. To determine the strength at which they produced equal hydrolytic effects, the stronger acids were diluted, until, in each case, the activity was equal to that of the weakest. The results were as follows:—

Table II.

$\text{HNO}_3 + 55.5\text{OH}_2$	468		
$\text{HCl} + 55.5\text{OH}_2$	499	+ $6\text{H}_2\text{O}$	436
		+ $3\text{H}_2\text{O}$	469 : 471
$\text{H}_2\text{SO}_4 + 55.5\text{OH}_2$	552	+ $8\text{H}_2\text{O}$	461
		+ $7\text{H}_2\text{O}$	469 : 469

The relative values thus arrived at,



are entirely rational; but as we have no means at present of determining the value of x in the case of nitric acid, the actual extent to which the various acids may be regarded as "hydrated" in solution is uncertain.

To determine the extent to which their activity is reduced by dilution, the rate of inversion was determined in solutions containing 1/10 and 1/20 of a gramme-molecular proportion of acid per 1000 grammes of water. The velocity constants arrived at are recorded in Table III.

Table III.

Acid.	1/10 N.			1/20 N.
	I.	II.	Mean.	Mean.
HNO_3	32.6	32.6	32.6	15.8
HCl	34.2	33.8	34.0	16.7
H_2SO_4	43.1	42.9	43.0	21.1

It will be seen that, in the dilute solutions, the difference between nitric and chlorhydric acids is slightly less than in concentrated and that the activity of sulphuric acid is far less impaired by dilution than is that of the other acids, the difference between it and the other acids in dilute solutions being considerably greater than in concentrated. The differences between the acids in weak solutions are far beyond those to be expected on the assumption that the acids affect the concentration of the solution in the manner in which they affect that of the stronger solutions—by the withdrawal of water. It is especially noteworthy that the diminution in activity on reduction to decinormal strength is not proportional to the dilution but about 1.5 times as great, although on further dilution to 1/20 the reduction is about proportional to the dilution; it is therefore clear that water has a specific effect in diminishing the activity of the acid, this effect being least in the case of sulphuric acid and greatest in the case of nitric acid.

These differences in behaviour of the three acids are presumably of considerable significance, as throwing light on the process of hydrolysis, especially as showing that it is a process in which water and the hydrolyte are in competition and that the former is either more attractive of or has greater influence over the hydrolyst.

The discrepancy is far greater, however, when acids of equal conducting power are compared as to their hydrolytic activity.

To reduce the molecular conductivity of sulphuric acid to that of chlorhydric acid in a weight-normal solution, the strength of the solution must be raised until 2·15 gramme-molecular proportions are present per 1000 grammes of water; the hydrolytic activity of acid of this strength at 25°, determined in a solution containing half a gramme-molecular proportion of sugar, was found to be $K=1818$. An equally concentrated solution of nitric acid gave the value 1452; a similar solution of hydrogen chloride the value 1692.

In view of the difficulty of determining the rate when the change is proceeding rapidly, it may be desirable to place on record the values of the constant deduced at intervals of five minutes.

Table IV.

HCl.	HNO ₃ .	H ₂ SO ₄ .
1684	1456	1834
1692	1445	1828
1683	1458	1801
1697	1444	1819
1701	1450	1808
1701	1455	1827
1692	1456	1812
1699	1451	1807
1689	1451	1827
1677	1457	1818

In order that the various values may be compared, they are collected together in the following Table V:—

Table V.—Hydrolytic Activities of Acids at 25°.

	HNO ₃ .	HCl.	H ₂ SO ₄ .	
2·15 N*	675	787	845	
N	468	499	552	
N/10	326	340	430	
N/20	316	334	422	
Expressed as Ratios.				
2·15 N	144	157	153	
N	100	100	100	
N/10	69·6	68·1	77·9	
N/20	67·5	66·9	76·4	
—	100	107	180	Solutions of equal conductivity.
2·15 N	100	99	125	Solutions of equal concentration.
N	100	107	118	" " "
N/10	100	104	132	" " "
N/20	100	105	133	" " "

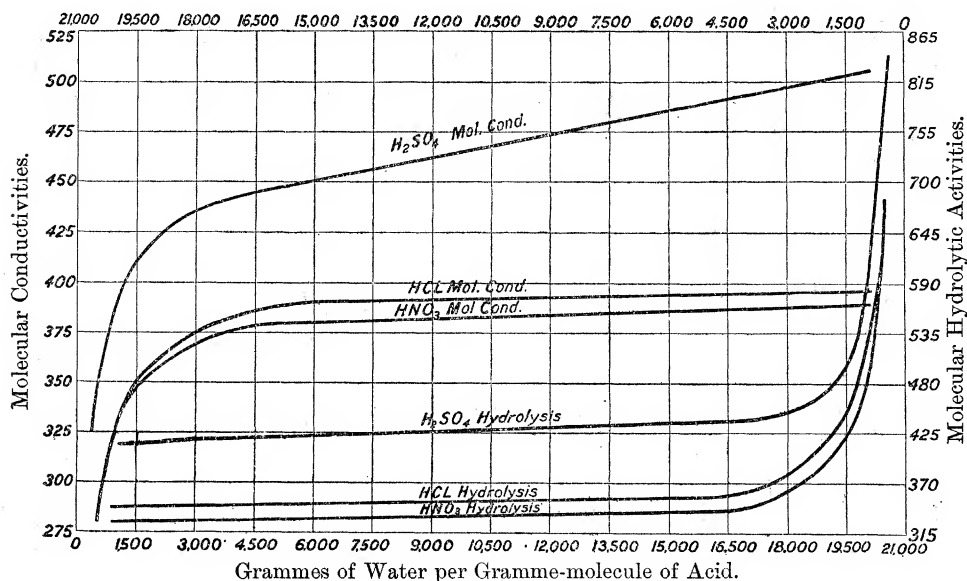
* The values in this section of the table are the molecular hydrolytic activities obtained by multiplying the observed velocity constants by the weight-normality factors in the first column.

The molecular conductivities at 25° of the various solutions used were found to be as follows :—

Table VI.

	HNO ₃ .	HCl.	H ₂ SO ₄ .	
2·15 N	281·6	278·7	330·4	Solutions of equal hydrolytic power.
N	329·4	330·0	395·6	
N + xH ₂ O	329·4	334·6	403·8	
(x = 0)		(x = 3)	(x = 7)	
N/10	383·1	391·6	468·9	
N/20	391·1	395·5	505·9	
Expressed as Ratios.				
2·15 N	85·5	84·4	83·6	
N	100	100	100	
N + xH ₂ O	100	101	102	
(x = 0)		(x = 3)	(x = 7)	
N/10	116	118	118	
N/20	119	120	127	
2·15 N	100	101	122	Solutions of equal hydrolytic power.
N	100	99	117	Solutions of equal concentration.
N/10	100	100	120	" " "
N/20	100	102	122	" " "
N/20	100	101	129	" " "

It is clear that the two methods afford very different results, dilution having a contrary influence on hydrolytic activity and on apparent molecular conductivity, diminishing the former and increasing the latter; specific differences are also manifest between the acids, nitric acid being most



sensitive to dilution, chlorhydric being affected to a slightly smaller extent and sulphuric very much less. The results are represented in a more obvious manner in the graph on p. 100. A point of some interest is the marked tendency to an alteration in the activity of chlorhydric as compared with nitric acid in concentrated solutions; this may be ascribed, with some probability, to the separation of hydrogen chloride from chlorhydric acid (HCl.OH_2) as the solubility limit of the former is approached and is a justification of the contention that two such substances are to be distinguished: in other words, of Lavoisier's conception of oxygen and of the now almost discarded view that oxygen is a constituent of all acids.*

In electrolysis only solvent and solute are reciprocally concerned, no substance entering into competition with the solute for the solvent; in hydrolysis the solvent influences both hydrolyte and hydrolyst, hence the difference in the phenomena.

Acids, presumably, have almost unlimited activity when highly concentrated, water playing the part of a mere catalyst, it may be supposed; the acid, on the other hand, is doubtless the effective catalyst in dilute solutions, to an extent which increases as the dilution is increased. The acid being shared by the water and the hydrolyte as the solution is more and more diluted, the competition for the acid between the water and the hydrolyte becomes more and more effective in that the hydrolyte suffers the most; indeed, it is probable that only a very small proportion of the total amount of acid present is effective, otherwise it would be difficult to understand why acids are so weak in comparison with enzymes.

The activity of enzymes is altogether extraordinary, a quantity of invertase, certainly less and perhaps considerably less than 10 milligrammes in weight sufficing to hydrolyse 21.3 grammes of cane-sugar dissolved in 250 c.c. of water within 30 minutes, whereas, in presence of one-fourth of a gramme-molecular proportion of hydrogen chloride (9.1 grammes), the same amount of sugar is hydrolysed only after about 48 minutes; using 0.91 gramme of the chloride, the complete change of the sugar is effected only at the end of about 14 hours, 30 hours being required if only 0.46 gramme of chloride be present. It is to be supposed that the colloid molecules of the enzyme have but slight mobility in solution, so that the sugar molecules must be pictured as attacking rather than as being attacked.

* [July 22.—Later observations confirm this conclusion and show that the conductivity of "hydrogen chloride" tends to lag more and more behind that of hydric nitrate the more concentrated the solution becomes. The hydrolytic values are not yet determined satisfactorily, as the rate of change is so rapid in concentrated solutions that it is difficult to obtain accurate results; apparently hydrogen chloride maintains its superiority. The scale of the graph is too small to show the differences in concentrated solutions.]

The nature of the processes involved in hydrolysis and electrolytic conduction is more fully discussed in the sixth of these communications.

VIII. *The Influence of Salts on Hydrolysis and the Determination of Hydration Values.* By H. E. ARMSTRONG and D. CROTHERS.

In the first of these communications a method was described which, it was suggested, permits of the evaluation of the average "concentrating effect" exercised by a salt in solution. The method involves the determination of the rate at which cane-sugar is hydrolysed by an acid alone, then of the rate at which it is hydrolysed in presence of a salt and finally of the amount of water required to reduce the rate of change in the presence of the salt to that at which it takes place when no salt is present; this amount of water is taken as the measure of the "concentrating effect."

Although, in the fourth communication, it was spoken of somewhat confidently as one which afforded a means of determining the *average degree of hydration* of a salt in solution, attention was specially called to possible limitations of the method. And in the fifth communication stress was laid on the fact that the solvent power of water is modified by dissolved salts presumably in a variety of ways—not merely by the withdrawal of a certain proportion in the form of water of hydration; moreover, this point of view had been specially developed by one of us in discussing the origin of osmotic effects.

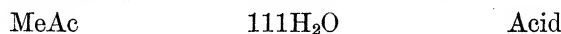
The results recorded in No. IV, relating to the hydrolysis of methylic acetate by chlorhydric and nitric acids in presence of corresponding salts, as was pointed out at the time, were of a somewhat remarkable character, the "hydration values" found for the salts being in all cases much lower than those obtained when using cane-sugar as hydrolyte. It is not to be denied that these departures were treated somewhat lightly; indeed, the assumption that the metallic salt entered into association with the ethereal salt, thereby hindering to some extent the association of the latter with the "hydrolyst," was referred to as being a simple explanation of the results, yet with the *caveat*: "we are not aware, however, that it has been suspected up to the present time that nitrates (the salts which gave particularly low values) are peculiarly active in thus combining." Our express object in making this statement was to imply that we doubted the sufficiency of the explanation.

The apparent "hydration values" deduced were as follows:—

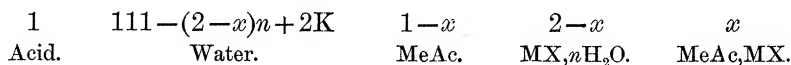
	Chlorhydric acid.			Nitric acid.	
	Sugar.	MeAc.		Sugar.	MeAc.
AmCl	10	5	AmNO ₃	7	-2
KCl	10	8	KNO ₃	8	1
NaCl	13	10	NaNO ₃	11	3

Assuming the degree of "hydration" of the salts to be the same in the presence of either hydrolyte, it should be possible from these results to approximate to the proportion of metallic salt associated with the methylic salt.

The rate of hydrolysis was determined in the system



It was then determined after adding two gramme-molecular proportions of salt, MX, to this system; and, finally, the mixture was examined containing 2K gramme-molecular proportions of water, K being the apparent degree of hydration of the salt MX deduced from the experiments. Assuming the actual degree of hydration (n) of the salt to be that found when using cane-sugar, writing x as the proportion of methylic acetate combined with the salt, the system in the solution would be:—



The rate of hydrolysis in this system being the same as that in the simple solution of acetate, water and acid, if the rate of hydrolysis depend on the ratio of MeAc to water, it follows that

$$\frac{1-x}{111 - (2-x)n + 2K} = \frac{1}{111} \quad \text{whence } x = \frac{2n-K}{111+n}.$$

The proportion of hydrolyte combined with the various salts in solution deduced with the aid of this equation is as follows:—

	Per cent.		Per cent.
AmCl	8.3	AmNO ₃	15.2
NaCl	4.7	NaNO ₃	13.1
KCl	3.3	KNO ₃	11.7

These values have a certain significance, although they involve the assumption that the actual hydration values of the salts are those found by means of cane-sugar and no allowance is made either (a) for the fact that the proportion of acid to ethereal salt in solution is not quite the same in the

presence as in the absence of the metallic salt or (*b*) for the water taken up by the ethereal salt and by the MeAc,MX complex or (*c*) for the possible combination of ethereal salt with the acid.

The order indicated is the same in both series, yet not quite that of the hydration values. It is obvious that ammonium nitrate—for which a minus “hydration” value was deduced—falls into line with the other salts; this salt, in fact, apparently differs less from the other nitrates than does ammonium chloride from the other chlorides. In the case of both chlorides and nitrates the ammonium salts have the greatest effect.

It is known that salts such as calcium chloride combine with methylic acetate and other ethereal salts and therefore are never used in drying them; it cannot well be supposed, however, especially in the case of the nitrates, that combination with the salt takes place *in aqueous solutions* of methylic acetate to such an extent as the calculation above made indicates. And on general grounds the apparent activity of the nitrates in comparison with the chlorides is altogether surprising—especially in view of the positive evidence brought forward in another communication (No. X) in which the combination of salts with cane-sugar in solution is considered—that chlorides are more active than nitrates. But if the values deduced do not afford a measure of the extent to which the salts considered combine with the acetate, they serve to indicate more or less clearly the manner in which the several systems are affected. The greater activity of the ammonium salts as well as of the nitrates in comparison with the chlorides is presumably to be correlated with the fact that the ammonium salts are present in solution to a larger extent than the other salts in the monadic form and that nitrates, in like manner, are probably less polymerised than chlorides.

It should be pointed out that the possible fixation of nitric acid by the salt, although not referred to by Armstrong and Watson, had been taken into account by them and put aside as an unlikely explanation of their results. It is true Ditte* has shown that both ammonium nitrate and potassium nitrate combine with nitric acid to form acid nitrates; apparently, however, the compounds are for the most part, if not entirely, decomposed by water; and sodium nitrate, which does not form an acid salt, is almost as active as ammonium and more active than potassium nitrate.

In the hope of obtaining further information as to the nature of the changes attending the admixture of the several substances in solution, the alteration in volume was determined which was produced by adding half of a gramme-molecular proportion (37.02) of methylic acetate to a solution containing a gramme-molecular proportion of salt together with 1000 grammes of water

* ‘Comptes Rendus,’ 1879, vol. 89, pp. 576, 641.

(a weight-normal molecular solution). It was to be supposed that if the salt combined to any considerable extent with the acetate there would be a corresponding alteration in volume and that chlorides would differ markedly from nitrates.

The results recorded in Table I were arrived at by determining the densities of the solutions and dividing the total weight of each solution by the density.

Table I.

$$\text{Methylic acetate } \Delta_4^{25} = \frac{0.880735}{0.880765} = 0.88075.$$

	Solution.		Solution + $\frac{1}{2}$ MeAc.		App. vol. of $\frac{1}{2}$ MeAc.	App. mol. vol. MeAc.	Alteration in mol. vol.
	Δ_4^{25} .	Volume.	Δ_4^{25} .	Volume.			
Water	—	1002.98	0.99777	1039.34	36.36	72.72	—
AmCl	1.01266	1040.34	1.01287	1076.70	36.355	72.71	-0.01
			1.01288	1076.69			
AmNO ₃ ...	1.02718	1051.53	1.02681	1087.97	36.405	72.81	+0.09
	1.02711	1051.61	1.02679	1087.98			
KCl	1.04146	1031.92	1.04090	1068.05	36.13	72.26	-0.46
KNO ₃	1.0553	1043.48	1.05402	1079.88	36.395	72.79	+0.07
			1.05403	1079.87			
NaCl	1.03611	1021.61	1.03569	1057.77	36.16	72.32	-0.40
NaNO ₃	1.05022	1033.22	1.04893	1069.75	36.52	73.04	+0.32
	1.05022	1033.22	1.04896	1069.73			

These results in no way serve to indicate that chlorides and nitrates in solution differ in any special manner in their behaviour towards methylic acetate, at all events to an extent which would serve to elucidate the very different extents to which the two classes of salts affect the rate of hydrolysis. At present, it is difficult to assign any special significance to the figures given in the last column of the table.

With the object of obtaining further information as to the manner in which chlorhydric and nitric acids and their salts influence one another in solution, we have determined the "molecular" electrolytic conductivities in solutions containing 1 gramme-molecular proportion of acid and of salt in 1000 grammes of water and have compared the values with those deduced on the assumption that the two substances retain their specific values; we have in this manner arrived at an estimate of the reduction in the conductivity value due to the admixture of salt and acid. The results are recorded in Table II (p. 106).

These results again serve to show that the difference between chlorides and nitrates is not of the order indicated by the difference in the hydration values deduced by the hydrolytic method, using methylic acetate as hydrolyte. Even if the diminution in conductivity be regarded as falling wholly on the acid

and it be supposed that the hydrolytic activity of the acid is diminished to the extent indicated, the hydration values obtained are in no way accounted for.

Table II.

	Molecular conductivity.		Diminution.	Diminution in molecular solution volume.	
	Observed.	Calculated.			
				c.c.	per cent.
HCl	329.23				
NaCl	85.91				
AmCl	111.73				
KCl	112.17				
HCl + NaCl	356.12	415.14	14.20	1.13	3.0
HCl + NH ₄ Cl	399.92	440.96	9.28	1.08	1.9
HCl + KCl	402.96	441.40	8.71	0.53	1.1
HNO ₃	323.49*				
NaNO ₃	76.32				
KNO ₃	82.84				
AmNO ₃	100.95				
HNO ₃ + NaNO ₃	345.20	399.81	13.66	1.59	2.6
HNO ₃ + KNO ₃	374.50	416.33	10.05	1.20	1.7
HNO ₃ + AmNO ₃ ...	385.60	424.44	9.11	1.02	1.3

* Owing to an oversight the nitric acid used was slightly below normal strength—a weight-normal solution gave the value 329.4.

To test the influence of the non-electrolyte on each constituent separately of the acid-salt pair, the “molecular” conductivity was determined of acid and salt in weight-normal solutions in presence of a molecular proportion of methylic acetate. The results are recorded in Table III.

Table III.

	Observed molecular conductivity.	Diminution.
		per cent.
HCl + MeAc	300.59	8.7
NaCl	76.14	11.4
KCl	98.87	11.8
AmCl	98.70	11.6
HNO ₃	292.4	9.5
NaNO ₃	69.63	8.8
KNO ₃	84.21	9.3
AmNO ₃	92.56	8.3

The differences observed between the two classes of salts are again insufficient to afford the desired explanation of their peculiar influence on hydrolytic activity as determined with the aid of methylic acetate.

Assuming that the reduction in conductivity is at least in part due to the reciprocal "dehydrating" influence which the two substances exercise in solution upon one another, the attempt was made to evaluate this dehydrating effect by determining the change in conductivity produced by diluting the solutions. The results obtained are recorded in Table IV. The results do not in any way correspond with those obtained by the hydrolytic method; it is clear that the effect on electrolytic conductivity produced by the admixture of several substances in solution cannot be balanced by the addition of water in the way that the "dehydrating" influence of a salt on the hydrolytic activity of an acid can be annulled by dilution. Whether the substance added be an electrolyte or a non-electrolyte, it will be obvious from the results recorded in Table IV that some effect is produced whatever the dilution but that the effect diminishes as the dilution is increased.

Table IV.

Solution.	+0H ₂ O.	+4H ₂ O.	+6H ₂ O.	+10H ₂ O.	+20H ₂ O.	+40H ₂ O.	+55.5H ₂ O.
NaCl	85.91	86.65		87.767			
NaCl + MeAc ...	76.14	77.62	78.15	79.19			
NaNO ₃	76.32	77.39		78.25			
NaNO ₃ + MeAc	69.63	70.83		72.56			
NaCl + HCl ...	356.12						417.55
NaNO ₃ + HNO ₃	345.20						396.29
KCl + HCl	402.96			416.20	425.41		
NH ₄ Cl + HCl ...	399.92					438.47	

Such results afford proof which cannot well be gainsaid that electrolytic conductivity and hydrolytic activity are processes of a fundamentally different character—affected in opposite directions by changes in concentration or in the medium.

Although the conductivity of the system HCl + MCl in solution is below the sum of the conductivities of its components, its hydrolytic activity is much superior to that of the acid alone—in the case of cane-sugar and sodium chloride to an extent which is expressed by representing the salt as withdrawing 13/55.5 of a molecular proportion of water. But the hydrolyte is itself party to the production of the "dehydrating" effect. To evaluate approximately its influence on the electrolytic conductivity, the conductivity of the system HNO₃.NaNO₃ was determined in presence of glucose. Using molecular proportions of the three substances and 1000 grammes of water, the apparent molecular conductivity was found to be 261.9 or 345.20—261.9 = 83.3 units less than that of the salt-acid pair alone—a reduction of 24 per cent.

The effect of glucose on the conductivity conditioned by sodium nitrate and by sodium chloride was also determined in solutions containing gramme-molecular proportions per 1000 grammes of water: the reduction produced was found to be 27·4 per cent. in the case of the chloride and 22·8 per cent. in the case of the nitrate. Raffinose, $C_{18}H_{32}O_{16}$, was found to have a still greater effect, the conductivity in a solution of sodium chloride being lowered by one-third of a gramme-molecular proportion of this carbohydrate to 68, a reduction of 21 per cent.

The effect of glucose on conductivity is therefore approximately two and a-half times that of methylic acetate and the molecular effect of cane-sugar (as shown in Communication No. X) is $44\cdot6/27\cdot4$, whilst that of raffinose is about $63/27\cdot4$ that of glucose. The significance of such results cannot be overlooked.

It remains to consider what explanation can be given of the remarkable lack of similarity in the behaviour of salts when contrasted by the hydrolytic method, using cane-sugar and methylic acetate.

In view of the evidence now brought forward, it is difficult to arrive at any other conclusion than that the difference is attributable mainly to the peculiarities inherent in the acetate.

The theory put forward in the sixth communication (*ante*, p. 83) involves the assumption that interaction does not take place initially between the nominal hydrolyte and the nominal hydrolyst but between their *hydrolyated* molecules; on this assumption, the rate of change will depend largely on the proportion of the one or the other which is present in minor proportion in the hydrolyated state. If, then, it be supposed that the affinity of methylic acetate for water is very slight, there would be relatively few effective hydrolyated molecules present in a simple aqueous solution; these molecules, moreover, would be very unstable. One effect of adding a salt to the solution would be to concentrate it, as a certain amount of water would enter into combination with the salt and be withdrawn from the solution; the water would also be dissociated by the interposition of the molecules of the salt and the proportion of hydrol in it increased; and this hydrol, together with that attached to the salt, would exercise a more or less powerful dehydrolyating influence both on the hydrolyte and the hydrolyst.

The introduction of a salt into the solution should therefore reduce the proportion of effective molecules both of hydrolyte and hydrolyst; these, however, would be affected in different degrees, according to the stability of their composite molecules: the substance which held hydrol but loosely would be more seriously affected than one which held it firmly, so that the effect on

the acid would be relatively slight in comparison with that exercised on the hydrolated molecules of the ethereal salt.*

If this argument be a sound one, it is clear that the "hydration values" arrived at by the method now under discussion will vary from case to case and that the highest values will be obtained by using hydrolytes and hydrolysts which form relatively stable hydrols in solution. But as several factors are simultaneously operative in every case, *the values deduced will necessarily, in all cases, be apparent values only.* The argument is equally applicable to cryoscopic and other physical methods; as, in reality, all methods of determining such values involve the occurrence of chemical interchanges in solution.

As the influence of a salt or indeed of any third substance, however exercised, necessarily extends both to hydrolyst and to hydrolyte, the "concentrating effect," in some cases, may be such that the increased activity of the hydrolyst more than compensates for the diminished activity of the hydrolyte, whilst in others it less than compensates for the diminution; in the one case the added substance will raise, in the other it will diminish the rate of change. The results brought forward by Senter† may all be regarded from this point of view—they are in no way incompatible, as he suggests, with the conclusion that neutral salt action is due to combination between salt and solvent with consequent concentration of the solution. But "interaction" should be substituted in this sentence for combination, in order that it may be a proper expression of the facts; it has never been contended in these studies of the processes operative in solution that the effects are due to combination alone but, on the contrary, it has always been implied that the changes in the medium are also of supreme importance.

The view here put forward that methylic acetate is a very weak hydrolyte is in accordance with the recognised fact that the carboxylic acids are, with few exceptions, relatively weak acids. It is therefore to be assumed that they are present in solution to but a small extent in the form of hydrolated molecules and that these molecules are easily dehydrolated. As the passage from water to alcohol and ether involves a great diminution in the activity of the compound, it is to be supposed that the introduction of a hydrocarbon radicle in place of the carboxylic hydrogen in acids necessarily conditions a great reduction in the activity of the compound: evidence that this is the case may be found in the simple fact that whilst acetic acid is miscible with water in all proportions, methylic acetate is but moderately soluble.

The superior activity of chlorhydric acid and chlorides in comparison with

* From this point of view, the comparison of the methylic salts of the various substituted acetic acids with methylic acetate will be of importance.

† 'Chem. Soc. Trans.,' 1907, vol. 91, p. 460; 'Proceedings,' 1908, p. 89.

nitric acid and nitrates may therefore be explained as a consequence of the presence of a larger proportion of the former in solution in the form of hydrolated molecules, the which molecules are also of a higher degree of stability than the corresponding nitrate-hydrols.

Experiments which are being carried out by G. Roche-Lynch show that the hydrolytic activity of bromhydric acid, as tested by means of cane-sugar, is considerably superior to that of chlorhydric acid. Nevertheless, the bromides apparently do not exercise a proportionately greater concentrating effect than corresponding chlorides—although, being salts derived from a stronger acid, they might all be expected to exhibit higher hydration values than the chlorides. The method used, however, is one involving competition between acid and salt and the strong acid may be expected to resist dehydro-lation more than a weaker acid can at the instance of its salts.

To give another instance, it was shown by W. H. Glover and one of us in a recent communication to the Society on the Hydrolysis of Raffinose that the cane-sugar section of the molecule is less readily hydrolysed than is cane-sugar itself. The difference may be explained on the assumption that raffinose is the weaker because it is a less hydrolated hydrolyte: experiments made recently by Dr. Glover seem to show that this is the case, as the “hydration value” of sodium nitrate determined by hydrolysing raffinose by nitric acid in presence of sodium nitrate is $8\text{H}_2\text{O}$ instead of $11\text{H}_2\text{O}$, the value arrived at by R. Whympers by means of cane-sugar.

But that salts are in a sense hydrated in solution there can be no doubt. To evaluate the effect which a salt produces apart from that arising from the mere combination with it of a certain amount of water, it may suffice to compare the action of a salt which apparently is but slightly hydrated with one which seems to be highly hydrated—silver nitrate and sodium nitrate, for example. The apparent hydration values obtained by the sugar method for these two salts are respectively $5\text{H}_2\text{O}$ and $11\text{H}_2\text{O}$. It may be supposed, on account of its low fusing point and its great solubility, that silver nitrate is present in solution to a large extent in the form of simple molecules (monads), probably to a greater extent than is sodium nitrate; the silver salt must, *ex hypothesi*, be hydrated to some extent; but even allowing that approximately only a single molecule of hydrone is attached to it, about four remain as the measure of the influence on the “osmotic” properties of the solution which is produced by the interposition of its molecules among those of the solvent and *the consequent dissociation* of the latter. Assuming it to be present largely in the monadic form, no other salt is likely to produce a much greater “mechanical” effect by the interposition of its molecules between those of the solvent. If, however, four molecules of hydrone be allowed as

the measure of the mechanical interference of a binary salt, it follows apparently that the sodium nitrate molecule is associated with hydrone to the extent of at least $11-4=7$ molecules. The argument is one to be considered carefully but before it be accepted as final it will be necessary to take into account the possible influence of the degree of intensity of the affinity of a salt for water—whether a salt which has a great affinity for water does not exercise a quasi-mechanical influence, extending beyond the molecules of hydrone which may be regarded as actually linked to its molecules, in proportion to its affinity for hydrol and hydrone, the which influence is necessarily included in any measurement made of its concentrating effect.

In any case, inasmuch as a salt undoubtedly exercises an effect which is the equivalent of a more or less considerable dehydrating or concentrating effect, it is a matter of convenience to express the magnitude of the influence it exercises in a particular system in terms of hydrone molecules, as though these were attached to the salt, although the value thus assigned may differ somewhat widely perhaps from the actual hydration value of the salt, if indeed it have any steady state of hydration—for it may well be that an influence is alone measured.

The argument which is here used in explanation of the effect of salts on hydrolytic activity may also be applied to the results recorded in Tables II, III, IV, showing the effect of admixture on electrolytic conductivity in solutions. Regarding the hydrolated molecules and their isodynamic congeners as the effective carriers of the current, it is to be supposed that owing to the interactions which take place between the composite molecules formed from the admixed solutes and to the change in the state of dissociation of the water conditioned by their joint presence, the proportion of effective molecules is reduced and consequently the conductivity is more or less diminished. From this point of view the effect produced by methylic acetate is to be regarded as almost entirely mechanical, in the sense that it is conditioned by alterations in the state of dissociation of the water consequent on the interposition of the neutral acetate molecules between those of the solvent.

It is noteworthy that the effect of dilution on the acid-salt mixtures is much greater than on those of salt with methylic acetate; probably, in the former case, the acid and salt are present in combination to some extent and water exerts a decomposing influence on the complex.

The larger diminution effected by glucose and the still more striking diminution produced by cane-sugar and raffinose may be in some slight degree ascribable to the formation of compounds with the salts; but such molecules must be thought of as exercising their chief influence in virtue of

the presence in them of long chains of attracting oxygen atoms, so that they act not only mechanically but also by exerting a direct dehydrating effect.

IX. *The Determination of Optical Rotatory Power.* By R. J. CALDWELL, D.Sc. (Leathersellers' Company's Research Fellow), and R. WHYMPER (Salters' Company's Research Fellow, City and Guilds of London Institute, Central Technical College).

It is known that to determine specific rotatory power to within 1 part in 10,000 it is necessary that the angle measured should exceed 100° , as the method of comparing tints with a triple field polarimeter of the Landolt-Lippich type cannot be relied upon to reveal differences of less than $0^\circ.01$. Moreover, as the late Sir William Perkin has specially pointed out, the accurate determination of large optical rotations is rendered difficult by the circumstance that the light from a sodium flame is contaminated with light of longer and shorter wave-lengths: light waves of various refrangibilities being unequally rotated by the sugar at the point of minimum luminosity in yellow light, the observer is confronted with the almost impossible task of matching a blue with a red field. The method of purifying light by liquid filters or gelatin screens recommended by Lippich* is not only imperfect but also involves so great a reduction of the illumination that difficulty is experienced in taking readings. Purification by spectroscopic means, as carried out by Abney,† is open to the same objection.

Perkin, using a two-field polarimeter, was able to overcome the difficulty by placing a direct-vision spectroscope in front of the eyepiece and made use of this method in his latest determinations of magnetic rotatory power.

In the course of an inquiry into the influence of salts on the rotatory power of cane-sugar, the results of which are discussed in the next communication, we found—especially when using strong solutions—that it was impossible to make satisfactory measurements on account of the colour difficulty referred to above. We were thus led to adapt Perkin's device to a triple-field Landolt-Lippich instrument and to introduce other improvements which have enabled us to overcome practically all the difficulties which ordinarily attend the determination of rotatory power.

The instrument modified was a triple-field Landolt-Lippich polarimeter, graduated to read, with the aid of verniers, to $0^\circ.01$ and constructed to carry tubes up to 600 mm. in length; the alterations were made by Messrs. A. Hilger and Co. at a moderate cost.

* 'Zeit. für Instrum.,' 1892, vol. 12, p. 340.

† 'Phys. Soc. Proc.,' 1885, vol. 7, p. 182.

The Jellett-Cornu instrument (purchased from Duboseq many years ago) used in carrying out the work described in previous communications has been modified in a similar manner with equal success.*

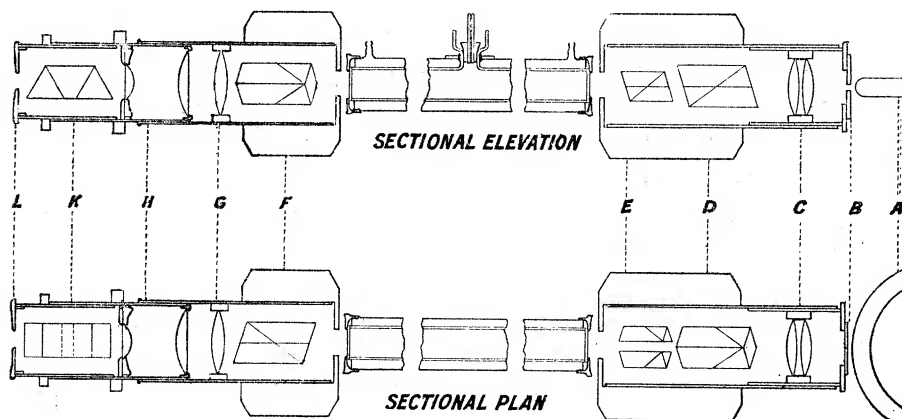


FIG. 1.

In the modified instrument, light from a lamp A passes through a horizontal slit B, which is permanently focussed by means of the achromatic lens C on the half-shadow field E of the polariser D. The slit B can be opened symmetrically and is usually adjusted to a width of 2 mm., so that the setting is made by observation of a band of light across the middle of the ordinary circular field occupying about a quarter of its area. This reduction has in no way rendered the instrument more difficult to use but it should be mentioned that it has been found undesirable to reduce the width of the slit to any greater extent.

A small three-prism combination, mounted in a brass tube, is fitted in front of the eyepiece in such a way that the spectrum can be brought into vertical alignment whatever the position of the analysing nicol. This prism has an angle of dispersion from C to G of about 16° . As the combination is adjusted to give no deviation with the D line, it is necessary to make the aperture L somewhat large, in order that readings may be taken over the whole of the visible spectrum.

If the prism K be sufficiently short, no alteration is necessary in the lenses supplied with the eyepiece.

Sodium Lamp.—The ordinary forms of sodium light are insufficiently bright for observations through 600 mm. of strong sugar solution. Doubtless

* In this instrument, a slit of fixed width previously determined to be suitable is arranged in front of the polarising nicol at E; being practically in the half-shadow field, this slit is permanently in focus, consequently the long tube carrying an achromatic lens at C of the other instrument is therefore unnecessary.

the lamp described by Sir William Perkin would serve in such a case but this is somewhat too expensive for general use, as it involves the use of a large platinum boat and of compressed oxygen. We found that a very bright flame could be obtained by passing finely powdered sodium carbonate into a blowpipe flame along with the air supply. This method, however, necessitated constant use of the bellows during the readings, and gave a light of constantly varying intensity. Ultimately a very cheap and simple instrument was devised, giving a bright and constant light. A Mecker burner (fig. 2) of the larger size was taken off the ordinary base, screwed on to a

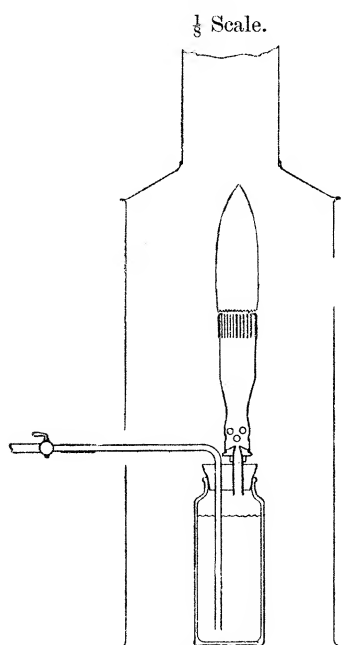


FIG. 2.

piece of brass tubing, $\frac{1}{4}$ inch internal diameter and $1\frac{1}{2}$ inches long and fixed in an ordinary glass bottle by means of a rubber stopper. The gas supply is led into the bottle by the glass tube and passes through the powder to the burner; this powder consists of an intimate mixture of equal weights of finely ground, dry sodium carbonate and clean sea sand, the bottle being filled to within 2 inches of the neck. The admixture with sand is necessary in order to prevent the particles of sodium carbonate from caking together and consequently affording a permanent passage for the gas: on account of its high density no sand is carried forward into the burner.

So great is the amount of sodium carbonate blown up, that the whole flame (6 inches \times $1\frac{1}{4}$ inches) is uniformly coloured an intense yellow; it has about 60 candle power in a horizontal plane and can be maintained at this intensity during at least an hour if the bottle and burner be occasionally shaken.

It is essential that a chimney should be arranged over the burner to carry off the sodium carbonate dust. The form of chimney we have used is shown in the figure; this has the additional advantage that it prevents light from escaping into the room.

In measurements with sodium light the difficulty always arises that the "optical centre of gravity" of the two D lines varies when the intensity of the light varies;* hence, measurements of the rotatory power of a substance in lights of different intensity will differ among themselves. The Arons-Lummer

* See Schönrock, 'Zeits. für Instrum.,' 1897, vol. 17.

mercury vapour lamp has been condemned by Landolt for similar reasons. In our experience, the form of the mercury vapour lamp patented by Bastian not only gives a light of constant intensity within the pressure limits of an ordinary 200-volt supply but is eminently suitable for polarimetric measurements with the spectroscopic arrangements we have described.* We have used the circular form of lamp shown in fig. 1 but a straight tube would undoubtedly be more convenient. When the lamp is burning the mechanism must be tilted slightly to bring the tube into a horizontal plane and it can be brought within $\frac{1}{4}$ inch of the horizontal slit on the polarimeter. The measurements recorded subsequently were made with a circular lamp which was so placed that light from both sides of the circle entered the slit.

The dispersive power of the prism is not sufficient to separate the two bright yellow lines $579\mu\mu$ and $576.9\mu\mu$. Fairly accordant measurements of rotatory power can be made with this yellow colour, the two lines together appearing to behave as if they had a wave-length $578\mu\mu$. When very large rotations are measured, the rotatory dispersive power of the substance is so great that the lines are separated and distinct differences in colour are noticeable between the several parts of the field. For this reason the measurements made with the yellow mercury lines represented in the tables under $[\alpha]_Y$ are not so trustworthy as those made with sodium light $[\alpha]_D$ or mercury green light $[\alpha]_{Hg}$.

The violet line ($435.9\mu\mu$) affords a light which it is difficult to utilise with our arrangements because the green and yellow which are seen at the same time are comparatively so much brighter and injuriously affect the sensitiveness of the eye. The green light ($546.1\mu\mu$) which is afforded by the mercury spectrum is in every way suitable for polarimetric work, and offers considerable advantages over sodium light on account of its brightness, purity, and constant intensity.

There are six other lines in the neighbourhood, but they are so faint that they could not be seen in our polarimeter at the zero point, even when the slit was closed to the ordinary spectroscopic width. That these lines are negligible is demonstrated by the fact that there is not the slightest indication of any difference in colour in the triple field, with the largest rotation we have measured, viz., 150° . In all cases the light is of such intensity that observations are easily made through tubes 600 mm. long; series of ten settings of the analyser have seldom shown a greater variety among

* After long use (perhaps 1000 hours) the lamp is noticeably deteriorated, inasmuch as the yellow light is more intense and the green relatively less intense than in the case of a new lamp.

themselves than 0°02. We regard the measurements we have made with this colour as the most trustworthy of all.

Method of using Instrument.—The glass caps for the polarimeter tube should be carefully tested and proved to be optically inactive under the greatest stress to which they can be subjected by the screw caps. Every precaution must be taken to prevent the glasses from being scratched. The solution is poured into the tube by the side opening, which is preferably closed with a small rubber stopper bearing a fine capillary tube, as shown in fig. 1, no air space being left into which the liquid can evaporate.

Although the effect of change in temperature on the rotatory power of cane-sugar is but small, the temperature must be maintained constant in the tube, as variations cause changes in the density and refractive index, thus rendering focussing difficult and the readings uncertain. The thermostat described by Lowry* has been found to give satisfactory results when an "Albany" rotatory pump is substituted for that he recommended.† Water at 25° is easily circulated through the jacket of a 600-mm. tube at about 1500 c.c. per minute.

Using sodium light, it is necessary to set the polariser at an (half-shadow) angle of about 8°, in order to secure sufficient illumination when using a long tube filled with a solution of sugar. Using the mercury green light and a 200-mm. tube, it is possible to adjust to a smaller half-shadow angle, and thereby increase the accuracy of the observations. The readings are taken in the ordinary way, with the exception that instead of comparing the sections of a complete circle, three squares of equal size are compared across the middle of the ordinary circular field. In observing rotatory power, the refracting prism must be adjusted so that the spectrum is vertical after the analyser has been brought approximately into the correct position for taking the readings.

On referring to Tables I, VI, VIII, IX, and X in the next paper, it will be seen that the "dispersion," viz., the ratio $[\alpha]_{\text{Hg}} \div [\alpha]_{\text{D}}$, is remarkably constant, being apparently unaffected by changes in the concentration of the sugar, or by foreign substances.

The green mercury light offers so many advantages in practice over sodium light, on account of its intensity and constancy, and because it is less tiring to the eye, requiring, moreover, neither adjustment nor attention, and being

* 'Faraday Soc. Trans.,' 1907, vol. 3, p. 11.

† This pump, which is made entirely of bronze, possesses the advantage that it runs silently and smoothly as a suction pump, even with a considerable load, and shows no sign of deterioration after six months of continuous use. The pump recommended by Dr. Lowry soon became unworkable, partly by rusting and partly by friction of the moving parts under the strain of sucking water through the jacket of a long tube.

free from fume or dust, that it may confidently be recommended for general use with any half-shadow polarimeter, modified in the manner described. In commercial work with sugar, readings could be multiplied by the factor 0.8486, or a scale might be specially calculated for use with green light.

- X. *The Changes effected by the Reciprocal Interference of Cane-sugar and other Substances (Salts and Non-electrolytes) in Aqueous Solutions.* By R. J. CALDWELL, D.Sc. (Leathersellers' Company's Research Fellow), and R. WHYMPER (Salters' Company's Research Fellow, Chemical Department, City and Guilds of London Institute, Central Technical College).

The experiments which are described and discussed in this communication were made primarily in the hope of further elucidating the manner in which salts exercise their well-known influence when used together with an acid hydrolyst in effecting hydrolysis; they are an extension of the observations recorded in Parts I and III of this series.

The action of acids alone as well as in presence of their salts on cane-sugar having been determined, it was desirable that the effect produced by salts alone should be studied systematically, as although the subject has already attracted much attention none of the numerous investigations* hitherto made has been carried out in such a way—with proportions which are equivalent—that the results with different salts are comparable; they cannot, therefore, be made use of for the purpose we have in view.

The considerable acceleration in the rate at which sugar is hydrolysed in presence of salts has been regarded by us in our previous communications as a *concentration effect* produced by the withdrawal from the sphere of action of a certain proportion of water molecules; we therefore, in the first instance, sought to ascertain whether the changes in the rotatory power of cane-sugar in solution conditioned by salts might, in like manner, be regarded as due to changes in the concentration. We feel obliged to conclude that this is not the case, since we find that the effect produced by a salt cannot be cancelled by dilution, except by adding a quantity of water altogether out of proportion to that which it is reasonable to suppose could be withdrawn by any salt; moreover, the reduction effected is in all cases greater than would correspond to the withdrawal of the whole of the water.

Having arrived at this conclusion, we were led to undertake the comparative study of the alterations in a number of the properties—specific

* Admirable summaries of these are to be found in Lippmann's 'Die Chemie der Zuckerarten,' vol. 2, pp. 1182—91.

rotatory power, density, volume and electrical conductivity—produced by associating cane-sugar with various substances in solution, from the point of view that combination takes place between the two substances; the extent to which this assumption is permissible will be discussed later on in considering the data. We are able to place on record the results of the examination of over 50 separate pairs, all of which have been prepared and measured with the greatest care. The material thus accumulated affords, for the first time we believe, an opportunity of discussing with some approach to certainty the reciprocal effects produced in aqueous solutions by cane-sugar and salts or non-electrolytes; it should be of value also in view of the known importance of salts as factors in vital metabolism and our complete ignorance of their function.

Preparation of Solutions.—The sugar used was that sold as *Coffee Sugar* or *Centrifugals*. This, it is well known, consists for the most part of large, well-formed crystals and is remarkable on account of the high degree of purification attained to in its manufacture. At first this sugar was used as purchased but subsequently, throughout the greater part of the inquiry, care was taken to remove all small particles from the large crystals by sifting and to use these latter alone (*cp.* footnote, Table I).

The salts and other substances used were all carefully purified materials, free from acidity.

The solutes were weighed out in a conical flask, due allowance being made for the air displaced. Approximately the right quantity of boiled distilled water was then run in and the solid dissolved by gently warming the flask. After cooling to the temperature of the room, the weight of the solvent was adjusted to the required amount on the balance. It was ascertained that no error was introduced by assuming that the air correction to be applied to the solution might be taken as the sum of the corrections on the constituent parts. As it was found to be necessary to minimise evaporation during filtration of the solutions, the operation was carried out quickly in a tube of the kind described by Lowry,* using three layers of filter paper strengthened with a piece of silk.

Determination of Rotatory Power.—The polarimeter used was the standard Landolt-Lippich triple-field instrument reading to $0^{\circ}01$, modified in the manner described in the previous communication. The measurements were all made in one water-jacketed tube 600 mm. long, care being taken always to use the same pair of optically inactive glass caps. The half-shadow angle was set to 8° and the slit adjusted to a convenient width at the commencement of the series of measurements, remaining untouched throughout, so

* 'Chem. Soc. Trans.,' 1904, vol. 85, p. 1558.

that the zero determined before each reading of a solution showed only the slight change due to the variation of the "personal error" from day to day. Occasionally, for the same cause, the zero for one colour would differ slightly from that for another colour. The zero of the instrument was determined to be the same whether the tube were empty or filled with distilled water at 25° the temperature at which all the measurements were made.

Determination of Density.—The form of Sprengel tube shown in fig. 1 has been found to be a specially convenient one in use; it has the advantage of being strong and easily wiped and of having no ground-glass joints. The liquid is drawn in through the tube A, the vessel being filled about to D. It is then placed in a thermostat maintained at 25° by means of a Lowry spiral thermo-regulator containing toluene. After about five minutes it is filled to the point B, by bringing some of the liquid contained in a small tube up to the point A and sucking gently at C. When the temperature has attained to constancy, as evidenced by the cessation of movement of the thread of liquid in the capillary tube DC, the liquid is very readily adjusted to the mark B by cautiously applying a piece of filter paper to the point A. The whole

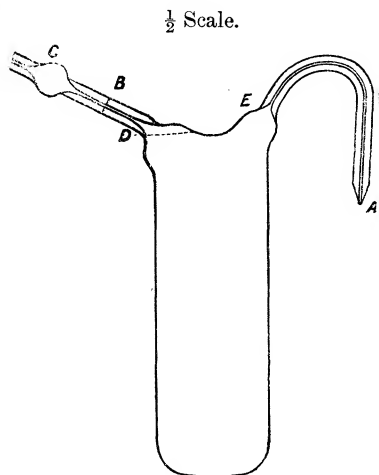


FIG. 1.

of the liquid is at the temperature of the bath except the negligible quantity in the capillary tube A. When the liquid is gently sucked back into the bulb C from the capillary tube AE, the surface tension of the film at E is sufficient to prevent the liquid from running back by gravity to A. The tube is then removed from the bath, cooled in a beaker of water to the temperature of the room and weighed. In our experiments corrections were always made for the air displaced, the humidity of the air being assumed to remain constant at 3.4 mm. pressure of water vapour. Using a tube of 40 c.c. capacity, it is possible to obtain densities accurate to 0.00001. The tube is easily cleaned and is dried by rinsing it out with alcohol, then warming it and sucking a stream of air through it by means of a filter pump.

Measurement of Conductivity.—The measurements were made in a resistance vessel of the form shown in fig. 2. The electrodes G are held in position by platinum wires fused in at B. The platinum wires are soldered to stout copper wires CDK at C and the glass tubes HL are fused on to the tubes BL at L. Increased rigidity is afforded and the strain is avoided at the

joints B and C by filling up the tubes BH with molten paraffin wax. A piece of rubber tubing, HDK, fitted over the glass tube BH at H serves to insulate the copper wire from the water of thermostat. Sufficient liquid is introduced at E to fill the U-tube to the level AA and the vessel is closed by connecting its limbs by a piece of rubber tubing EFN. The vessel is immersed several inches below the surface of the water in the bath, hanging from the copper wires CDK which are slipped into the mercury cups MM in electrical connection with the Kohlrausch wheel-bridge.

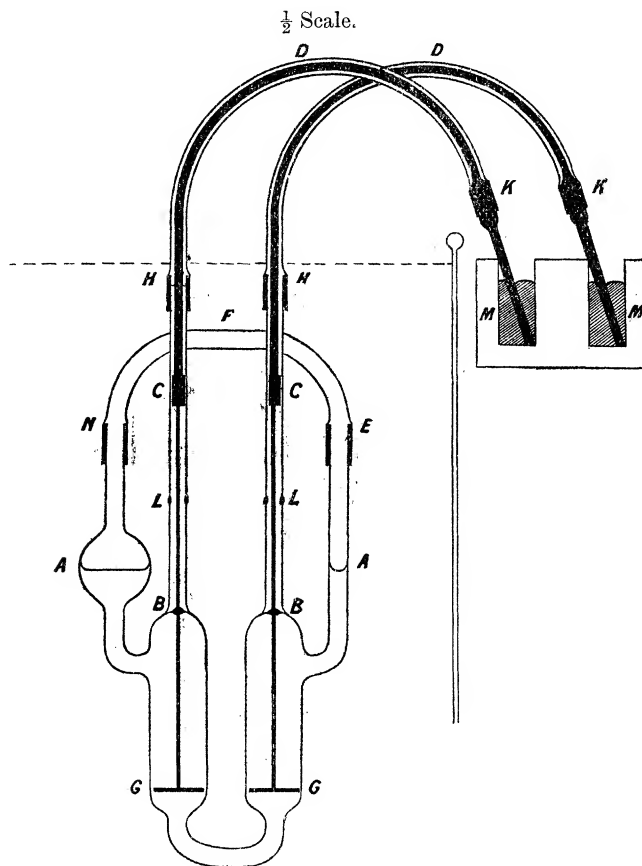


FIG. 2.

This arrangement has the advantage that the connections are made instantaneously without using screws; moreover, the whole apparatus is at the temperature desired, and there is no possibility of the liquid evaporating.

The readings were taken with a Kohlrausch wheel-bridge, inductorium and telephone, using the method described by Bousfield and Lowry.* The

* 'Phil. Trans.,' 1904, A, vol. 204, p. 286.

resistance of the electrolytic cell was as nearly as possible balanced by coils of known resistance wound non-self-inductively so that the readings could always be taken at points close to the middle of the wire. Due allowance was made for inequalities in the bridge wire, resistance of the leads and conductivity of the solvent. The water used was prepared by means of the Bousfield still;* its specific conductivity at 25° did not exceed 0.000002. The results are probably accurate to 1 part in 1000.

Specific Rotatory Power of Cane-sugar in Solution.—Although Tollens and several later observers have shown that the specific rotatory power of cane-sugar in solution increases very slightly on dilution, their observations were made under conditions somewhat different from those we have adopted. On this account and in order that we might know the exact behaviour of the sugar we were using, we have examined solutions of weight-molecular strength ($C_{12}H_{22}O_{11} : 55.5 \text{ OH}_2$) and those formed by adding an additional 40, 80 and 120 gramme-molecular proportions of water.

The results are recorded in Table I. The value deduced, $[\alpha]_D^{25} = 66^\circ 40$, for weight-molecular strength is in close agreement with that calculated by means of Wiley's temperature coefficient from Tollens' results— $66^\circ 36$; and in so far as the observations are concerned our results are in general agreement with those of other observers in showing a slight increase in the value on dilution.

It will be noticed that the dispersion ratio, $[\alpha]_{Hg}/[\alpha]_D = 1.178$, is practically the same in all solutions. This relation also holds good in all solutions we have examined of cane-sugar in admixture with salts or non-electrolytes (Tables I, VI, IX, XI); in discussing our results, therefore, we shall consider only the values obtained in green light. The one noteworthy point is the smallness of the change in the rotatory power of cane-sugar as the concentration is altered. It would seem probable, however, that the degree of association as well as the degree of hydration must vary somewhat as the concentration is varied and that these changes exert an opposing influence on the rotatory power, becoming imperceptible in consequence.

It is noteworthy that liquid ammonia and other anhydrous basic substances are good solvents of sugar and that in all cases the apparent rotatory power in such solutions is high. According to Wilcox,† in fact, sugar affords high osmotic values in solution in pyridine, pointing to association with the solvent. In solutions such as we have examined, the pyridine was in so much water that it is improbable that it produced any effect of its own by

* 'Chem. Soc. Trans.,' 1905, vol. 87, p. 740.

† Wilcox, 'Journ. Phys. Chem.,' 1901, vol. 5, p. 585; 1902, vol. 6, p. 341.

combining with the sugar. It is, however, by no means improbable that sugar is present in basic solvents to a more or less considerable extent in the form of complex molecules, bearing in mind the very high apparent specific rotatory power which it exhibits in such liquids.

Table I.—Specific Rotatory Power of Cane-sugar in Solutions of various Strengths. One gramme-molecule of cane-sugar dissolved in 1000 grammes of water (55·5 gramme-molecules), diluted with 40, 80 and 120 gramme-molecules of water.

Additional water.	Density of solutions.	$[\alpha]_{\text{Hg}}^{25}$		$[\alpha]_{\text{Y}}^{25}$		$[\alpha]_{\text{D}}^{25}$		Dispersion $[\alpha]_{\text{Hg}} \div [\alpha]_{\text{D}}$
		Experi- mental values.	Mean.	Experi- mental values.	Mean.	Experi- mental values.	Mean.	
Sugar "A."								
.....	1·10417	78·298	78·30	69·292	69·29	66·438	66·44	1·1785
.....	1·10416	78·293		69·293		66·433		
40H ₂ O ...	1·06450	78·311	78·29	69·299	69·28	66·468	66·46	1·1780
	1·06449	78·274		69·262		66·460		
80H ₂ O ...	1·04617	78·241	78·25	69·173	69·20	66·479	66·48	1·1770
	1·04619	78·253		69·224		66·491		
120H ₂ O ...	1·03571	78·270	78·28	69·211	69·25	66·509	66·51	1·1770
	1·03578	78·297		69·288		66·505		
Sugar "B."								
.....	1·10404	—	78·25			—	66·40	1·1785
40H ₂ O ...	1·06448	78·294 78·292	78·29			— 66·421	66·42	1·1787
80H ₂ O ...	1·04625	78·300 78·287	78·29			— 66·410	66·41	1·1789
120H ₂ O ...	1·03582	78·328 78·294	78·31			— 66·404	66·40	1·1794

The values recorded in this table were obtained at different times—the one set at the beginning, the other at the end of the inquiry. The quality of sugar sold as Centrifugals or Coffee Sugar was used throughout; this consists for the most part of large crystals mixed with a small proportion of fine material, which appears to be only in part the product of abrasion. Sample "A" (referred to in Tables I and IX) was used as purchased, but at an early stage it was noticed that the large and small crystals differed somewhat in rotatory power, thus—

Large crystals.....	$[\alpha]_{\text{D}}^{25} = 66·40$
Small „	66·53
Mixed	66·44

Sugar "B" consisted only of large crystals.

In presence of water, ammonia has an effect similar to, although very much weaker than, that produced by caustic potash or soda, reducing the optical activity to a very slight extent; the rotatory power of cane-sugar in liquid ammonia, however, is much higher—especially in dilute solutions—than in aqueous solutions, rising to $[\alpha]_D = 78^\circ$.* Other amines give similar values. As it does not appear probable that compounds containing the similar groups $O:OH_2$ and $O:NH_3$ would differ to any considerable extent in their optical effect, these high values are in favour of the assumption that cane-sugar is present in such solutions at least partly in an associated form which is more active optically.

It may be pointed out that our observations show that glycerol has a distinct negative influence. According to Seyffart† glycerol has no effect on the rotatory power of cane-sugar.

Influence of Non-electrolytes.

The obvious alterations conditioned in solutions of cane-sugar by non-electrolytes (Tables II, VI, VII) are slight, especially in comparison with those effected by salts. Except in the two cases of aldehyde and trichloraldehyde, the apparent specific rotatory power of the sugar in solution is scarcely affected. These compounds and perhaps acetone are, in point of fact, those which it is most likely would prove to be active;‡ it was scarcely to be supposed that the alcohols, methylic acetate or weakly basic substances such as urea and pyridine would tend to combine with sugar in presence of much water. Assuming—as contended in a recent communication to the Society by H. E. Armstrong and W. H. Glover, “On the Hydrolysis of Raffinose”—that the oxygen atom in the ring in the biose carbohydrate is the primary point of attack and the seat of combination, it is not improbable that aldehydes would combine with sugar and give rise to ethenoid

compounds of the type $\begin{array}{c} \text{C} - \text{C} \\ | \quad | \\ \text{C} \quad \text{C} \\ \diagdown \quad \diagup \\ \text{O} : \text{OCHR} \end{array}$; such compounds, it is to be expected,

would have an enhanced rotatory power, owing to the influence exerted by the ethenoid linkage.§ The difference in the optical change produced by

* Sherry, ‘Journ. Phys. Chem.,’ 1907, vol. 11, p. 559.

† Lippmann, p. 1181.

‡ It should be mentioned that reputed compounds of cane-sugar with aldehydes have been described by Schiff. According to Pottevin, the rotatory power is much increased by the addition of a considerable proportion of aldehyde.

§ Cf Armstrong and Robertson, ‘Chem. Soc. Trans.,’ 1905, p. 1272.

the two aldehydes is in no way surprising; and in view of this difference it is not improbable that acetone is also active in combining but that owing to its symmetrical character the optical effect is slight.

Table II.—Effect of non-Electrolytes on the Specific Rotatory Power of Cane-sugar in Relation to Volume Change in Solution, Gramme-molecular Quantities of each Solute being dissolved in 1000 grammes of Water.

Non-electrolyte.		$[V_{Aq+nE} - V_{Aq}]$ in c.c.	$[V_{Aq+nE+Sg} - V_{Aq+Sg}]$ $- [V_{Aq+nE} - V_{Aq}]$ in c.c.	Alteration in $[\alpha]_{D}^{25}$ in degrees.
	c.c.			
Acetaldehyde	(56·74)	43·06	0·00	+0·82
Methylic acetate...	(84·08)	72·43	-0·06	+0·11
Acetone	(73·79)	66·41	-0·16	+0·11
Methyl alcohol ...	(40·35)	38·17	-0·44	+0·10
Ethyl alcohol	(58·55)	55·21	+0·13	+0·08
Urea	(48·04)	44·46	+0·71	0·00
Pyridine	(85·55)	78·87	-0·25	-0·03
Glycerol	(73·14)	71·33	+0·44	-0·11
Chloral hydrate ...	(97·28)	93·08	-0·08	-0·58

NOTE : V_{Aq} = vol. of 1000 grammes water at 25° = 1002·98 c.c.

V_{Aq+nE} = vol. of solution of 1 gramme-molecule non-electrolyte in 1000 grammes water.

V_{Aq+Sg} = vol. of solution of 1 gramme-molecule sugar in 1000 grammes of water = 1215·68 c.c.

$V_{Aq+nE+Sg}$ = vol. of solution containing 1 gramme-molecule sugar, 1 gramme-molecule non-electrolyte, and 1000 grammes water.

The figures given in brackets are the actual volumes of non-electrolyte taken per 1000 grammes water.

When the changes in volume which attend the dissolution of the various non-electrolytes in water are considered (Table II, column IV) it is clear that compensating cross influences must be at work which mask the individual effects. The alcohols and pyridine are undoubtedly substances which are far more attractive of water than is methylic acetate; they should all produce somewhat similar effects in modifying the "osmotic properties" of the water and it is to be supposed that those which are the more attractive of water would exercise the greater influence. Yet, as a matter of fact, there is but a slight obvious change in volume on mixing the alcohols with water, whilst the dissolution of methylic acetate—the one neutral compound among the non-electrolytes studied—is attended with a great diminution in volume. It can only be supposed that the real effects are masked in

consequence of structural differences consequent on different modes of packing of the composite molecules which are formed in the solution.

It is important to notice that in the case of some of the non-electrolytes used in our experiments larger proportions than those we have taken are known to produce greater effects. Thus, according to Tollens, the values of $[\alpha]_D^{20}$ in the case of solutions containing 10 per cent. of sugar are:—

In water	66·67
In 1 part water and 3 of alcohol	66·83
" " methylic alcohol ...	68·63
" " acetone	67·40

As sugar is insoluble in ethylic and but very slightly soluble in methylic alcohol, it is scarcely probable that it combines with either; the greater increase in the apparent specific rotatory power conditioned by a large proportion of methylic alcohol is, therefore, presumably an indication that in such solutions the sugar is present in an associated, more optically active, form. The method adopted by Tollens of deducing the activity of cane-sugar *per se* by extrapolation from observations made with aqueous solutions would not necessarily afford a true value if the sugar complexes are largely, if not entirely, resolved when it is dissolved in water. Tollens, who used solutions containing at most about 70 per cent. of sugar, deduced the value 63·9; a somewhat higher value was deduced by Schmidt, who used solutions containing up to 85 per cent.; it is therefore more than probable that solid sugar has a higher rotatory power than has been supposed.

Influence of Electrolytes.

The effects produced on adding salts to solutions of cane-sugar are altogether remarkable in comparison with those exercised by non-electrolytes (Tables III, VIII, IX, X). In every case the apparent rotatory power of the sugar is somewhat diminished; the admixture of the salt in solution with the sugar in solution is always attended with a relatively considerable increase in the volume; and the conductivity of the salt in solution is diminished to a surprising extent by the addition of the sugar.

Change in Rotatory Power.—Taking into account the effect produced by the three classes of salts, the nitrates obviously exert a smaller influence than the chlorides, whilst the sulphates are more active than the chlorides; caustic alkalis are far superior even to the sulphates.

Inasmuch as compounds of sugars with salts have been isolated, there is every reason to suppose that combination can take place in solution between

Table III.—Effect of Electrolytes on the Rotatory Power of Cane-sugar in relation to the Volume Changes and the Conductivity of the Electrolytes in the Mixed Solutions. Gramme-molecular quantities of each solute dissolved in 1000 grammes of water.

Electrolyte.	Gramme-molecular weight.	$[V_{Aq} + E - V_{Aq}]$ in c.c.	$[V_{Aq} + E + Sg - V_{Aq} + Sg]$ in c.c.	Molecular conductivity of electrolyte in water alone.	Loss of conductivity on dissolving sugar per cent.	Diminution in $[\alpha]_{H_g}^{25}$ of sugar in degrees.
Ammonium nitrate	80.05	48.92	+1.15	100.95	42.8	0.19
Potassium nitrate	101.16	40.50	+1.52	92.84	43.7	0.44
Sodium nitrate	85.06	30.09	+1.73	76.32	43.8	0.53
Lithium nitrate	69.04	38.71	+0.96	56.58	44.1	0.21
Silver nitrate	169.94	30.97	+1.71	78.50	44.1	0.17
Calcium nitrate	164.12	73.46	+2.25	88.10	44.5	0.22
Strontium nitrate	211.62	49.24	+3.00	91.52	45.4	0.39
Ammonium chloride	53.49	37.42	+0.99	111.73	43.2	0.58
Lithium chloride	42.48	18.59	+1.20	73.43	44.4	0.63
Sodium chloride	58.50	18.58	+1.54	85.91	44.6	0.95
Potassium chloride	74.60	28.94	+1.40	112.17	44.6	0.83
Potassium bromide	119.11	36.09	+1.40	115.55	45.1	1.20
Potassium iodide	166.12	47.02	+1.06	118.34	46.2	2.18
Strontium chloride	158.50	53.60	+2.57	119.85	45.5	1.12
Calcium chloride	111.00	32.80	+2.02	123.67	46.6	1.29
Barium chloride	208.30	30.73	+3.35	138.94	47.2	0.55
Sodium sulphate	142.16	23.64	+4.33	94.86	47.4	2.17
Zinc sulphate	161.46	4.52	+3.63	46.78	51.1	1.08
Magnesium sulphate	120.42	6.66	+3.39	50.22	51.5	1.26
Sodium phosphate	142.11	12.31	+5.72	64.06	50.5	3.66
Potassium hydroxide	56.16	11.70	+3.92	185.57	75.6	7.65
Sodium hydroxide	40.06	-1.70	+3.39	151.23	79.5	7.60

salts and cane-sugar; it is to be expected, from this point of view, that nitrates would be the least and sulphates the most active. The high values obtained with alkalis are in accordance with the well-known behaviour of cane-sugar toward these compounds.

Although the optical values given in the last column of the table cannot be regarded as an absolute measure of the extent to which combination takes place, there can be little doubt that this is very nearly the case, inasmuch as the nitrates combine to the least and the sulphates to the greatest extent.

Assuming that the salt combines with the sugar in the manner supposed

above, forming compounds of the type $\begin{array}{c} \text{C}-\text{C} \\ | \quad | \\ \text{C} \quad \text{C} \\ \diagdown \quad \diagup \\ \text{O} : \text{XR} \end{array}$, the alteration in the optical

effect arises at the O : OXR junction. The effect of this junction will probably not be very different in a series of similar salts, as the modification induced by different metallic radicles is usually not very great; on the other hand, it is to be expected that the effect will vary somewhat more considerably as the negative radicle is varied.

Change in Electrical Conductivity.—The remarkable influence of sugar in reducing the electrical conductivity of salts in solution (Tables III, IV, V, XII), to an extent varying between 43 and 51 per cent., might be supposed to be mainly of a “mechanical” nature, *i.e.*, as in part due to direct obstruction of the current and in part to changes in the medium produced by the interposition of the molecules of sugar (*cf.* I, p. 282), particularly as the diminution is produced to much the same extent whatever salt be used.

Regarding the diminution in conductivity as made up of two factors, *viz.* (1) combination of the electrolyte with sugar, (2) mechanical effect of the sugar molecules; assuming, moreover, the latter to be independent of the electrolyte considered, the amount of compound should be deducible in the following manner.

If a per cent. of the salt be combined and presumably inactive in conducting the current and if b be the proportional decrease in conductivity effected in other ways by the sugar, the conductivity of the electrolyte in presence of sugar will be $(100 - a) \times b$ per cent. of its value in the absence of sugar.

The value of the factor b will vary greatly according to the concentration of the solution; but for the purpose of calculation it is assumed that at any particular concentration it is independent of the electrolyte considered. In weight-normal solutions b may be taken equal to x and in solutions diluted with 80 equivalents of water as y .

The factor a , *i.e.* the amount of compound, will be proportional in the case

Table IV.—Interference of Sugar and Salt in Presence of varying Quantities of Water.
One gramme-molecule of sugar and of salt dissolved in 1000 grammes of water
+ 0, 40, 80 or 120 gramme-molecules of water.

Salt.	Extra water.	$[V_{Aq+E} - V_{Aq}]$ in c.c.	$[V_{Aq+E+Sg} - V_{Aq+Sg}]$ $- [V_{Aq+E} - V_{Aq}]$ in c.c.	Loss in conductivity of salt per cent.	Diminution in $[\alpha]_{Hg}$ of sugar in degrees.
Sodium chloride	—	18.58	+ 1.54	44.6	0.95
	20H ₂ O	—	—	—	0.69
	40H ₂ O	18.35	0.88	29.3	0.51
	80H ₂ O	18.08	0.77	21.6	0.33
	120H ₂ O	17.95	0.73	17.2	0.23
Magnesium sulphate	—	6.66	+ 3.39	*51.5	*1.26
	40H ₂ O	4.47	2.29	33.9	0.80
	80H ₂ O	3.11	1.64	*25.4	*0.56
	120H ₂ O	2.28	1.71	20.7	0.43
Potassium nitrate.....	—	40.50	+ 1.52	43.7	0.44
	40H ₂ O	39.96	1.04	29.2	0.22
	80H ₂ O	39.68	0.41	21.7	0.15
	120H ₂ O	39.31	0.71	17.1	0.06
Potassium bromide ...	—	36.09	+ 1.40	*45.1	*1.20
	40H ₂ O	35.67	0.98	30.0	0.67
	80H ₂ O	35.52	0.48	*22.3	*0.46
	120H ₂ O	35.42	0.40	17.6	0.30
Potassium hydroxide	—	—	—	—	.7.65
	40H ₂ O	—	—	—	6.87
	80H ₂ O	—	—	—	6.43
	240H ₂ O	—	—	—	5.22

Table V.—Interference of Sugar and Salt dissolved in varying Proportions.
1.0, 0.2 or 0.05 gramme-molecule of sodium chloride dissolved in 1000 grammes of water with and without 1 gramme-molecule of cane-sugar.

Solute per 1000 grammes water.	Apparent molecular volume of salt in c.c.	Volume change per molecule salt in c.c.	Molecular conductivity.	Loss in conductivity per cent.	$[\alpha]_{Hg}^{25}$ in degrees.	Diminution in $[\alpha]_{Hg}^{25}$ in degrees.
1.0 gr.-mol. NaCl ...	18.58	1.54	85.91	44.6	—	0.95
1.0 gr.-mol. NaCl + 1 gr.-mol. sugar	20.12		47.610		77.30	
0.2 gr.-mol. NaCl ...	17.45	1.35	100.36	44.9	—	0.12
0.2 gr.-mol. NaCl + 1 gr.-mol. sugar	18.80		55.30		78.13	
0.05 gr.-mol. NaCl	17.0	1.4	111.12	45.9	—	0.05
0.05 gr.-mol. NaCl + 1 gr.-mol. sugar	18.4		60.13		78.20	

of varying amounts of any particular salt to the diminution in rotatory power of the sugar by the salt. Since, however, the rotatory power of the compound molecule may not be and probably is not independent of the nature of the salt, the factor a cannot be taken as quite proportional to the change in rotatory power in the case of different salts; a different factor (l , m) must therefore be used for each salt. By making use of the figures marked with an asterisk in Table IV, the four equations obtained are:—

$$\text{MgSO}_4 : (100-a)b = (100-l \times 1^{\circ}26) \times x = 100-51.5 = 48.5 \text{ per cent.}$$

$$(100-a)b = (100-l \times 0^{\circ}56) \times y = 100-25.4 = 74.6 \quad ,,$$

$$\text{KBr} : (100-a)b = (100-m \times 1^{\circ}20) \times x = 100-45.1 = 54.9 \quad ,,$$

$$(100-a)b = (100-m \times 0^{\circ}46) \times y = 100-22.3 = 77.7 \quad ,,$$

Solving these, we have

$$x = 0.370, \quad y = 0.662, \quad l = -24.5, \quad m = -40.4.$$

The values of l and m being negative are of an impossible character—a minus quantity of compound being inconceivable.

It is scarcely to be questioned that the first assumption is correct, namely, that the amount of compound of sugar with any particular salt is proportional to the effect produced by that salt on the rotatory power. The error must arise in assuming that the sugar produces a “mechanical effect” which is independent of the salt affected. In the case of barium chloride, to take an example, a large decrease in conductivity is associated with but a small change in the rotatory power and obviously such a result may be taken as confirmatory of this argument.

Although it is impossible apparently to deduce the extent to which combination takes place from a consideration of the conductivity values in the case of salts, a minimum estimate may perhaps be arrived at in the case of the caustic alkalis by another line of argument.

The very marked decrease in rotatory power produced by alkalis, whether ascribable or not to the formation of actual salts in which hydroxylic hydrogen is displaced by metal, must be regarded as evidence that “combination” takes place to a considerable extent, especially in view of the even more remarkable diminution of the conductivity in a solution of an alkali effected by cane-sugar. Assuming, in order to arrive at a minimum value, that the reduction in conductivity effected in the case of sodium chloride (44.6 per cent.) is wholly a mechanical effect and that the alkali is influenced mechanically to an equal extent, if x per cent. of the alkali enter into combination with the sugar, in the case of sodium hydroxide,

$$(100-x) \times (100-44.6)/100 = (100-79.5).$$

Since $x = 63$ per cent. it may be assumed that approximately this proportion of compound is formed.

On this assumption, the rotatory power would be decreased to $[\alpha]_D = 56^\circ$ if the sugar were completely combined with the alkali. It is noteworthy that the value $56^\circ.8$ has been deduced by Thomson by extrapolation from measurements made with proportions of sugar and alkali such as we used at various concentrations as that of the rotatory power of sodium saccharate in the absence of water.

Regarding the changes in rotatory power as directly proportional to the amount of salt entering into combination with the sugar, if the observed values are contrasted with those thus deduced for alkalis, it would follow that combination takes place to an extent approximating to 7 per cent. in a case such as that of potassium chloride and to 18 per cent. in the case of the iodide. If, however, the rotatory power of the compound formed by potassium iodide be greater than that of the corresponding compound with potassium chloride, this latter estimate will be subject to more or less considerable reduction. The uniformly low values given by nitrates are in accordance with this line of argument, as nitrates are generally regarded as less prone to enter into combination than chlorides.

Far more striking than the effect produced on the sugar by the salt, as indicated by the change in rotatory power, is the surprising diminution by almost one-half in the conductivity of salts in solution which is determined by the sugar—especially when it is considered that this diminution is brought about by the addition of a single molecular proportion of a substance like sugar, ordinarily regarded as a somewhat inert compound, to a mixture of a single molecular proportion of salt with 55.5 molecular proportions of water.

The effect cannot be in any way accounted for by supposing that the salt and sugar enter into combination to the extent required by such an assumption—probably, at the very most, about one-fifth of the change can be ascribed to such an action. It has already been shown, in the first of these communications, that glucose and galactose reduce the conductivity of solution of hydrogen chloride to the extent of about 30 per cent. As it is to be supposed, on general grounds, that the glucoses would combine even more readily than cane-sugar with acids and salts, bearing in mind the manner in which the glucoses are related to cane-sugar, there can be little doubt that the remarkable influence sugars exercise on conductivity is to be correlated with the presence in them of a series of oxygen atoms, the effect being practically proportional to the number of hydroxyl groups (8 and 5) present in the two carbohydrates.

The differences noticeable among the various salts are doubtless ascribable to the differences in the extents to which the salts exist in solution in the monadic form, as well as to differences in the extent to which they enter into combination with the sugar, also to specific differences among the salts affecting conductivity.

The substances most affected, such as barium chloride and zinc and magnesium sulphates, are compounds which are near the saturation point in solutions such as were examined and it is probable that these salts readily undergo polymerisation in such solutions. Apart from these three salts, the order in which conductivity is affected is practically identical with the order of change in rotatory power.

Volume Changes.—As shown in the column B—A in Table XII, the admixture of sugars with salts in solution involves, in all cases, a more or less considerable expansion. This result is especially striking in view of the fact already commented on that non-electrolytes, as a rule, do not produce such an effect. There is reason to suppose that the increase in volume is due, at least mainly, to the liberation of water; also that this is conditioned less by the interaction involved in the combination of sugar with salt than by the change in the medium brought about by the increase in the amount of solute which is a necessary consequence of the admixture of the two substances. The change in volume is deduced by a method of comparison which is faulty in that the double effect on the medium, due to the presence of the two solutes in solution, cannot be taken into account. Thus the values in column A are the apparent volumes of the salts in solution in water, those in B the apparent volumes of the salts in solution in presence of sugar: in a solution, therefore, which differs from water in having sugar present in it; the values given in the column B—A are in defect, therefore, to the extent of this difference.

It is noticeable that specially high values are given by salts such as barium chloride and the sulphates. It may be supposed that barium chloride is present in an ordinary aqueous solution, at least to a considerable extent, in a hydrated form; and that on the addition of sugar much of the salt present in this form becomes polymerised, losing water in the process. A similar explanation applies to the sulphates.

On reference to Table IV, it will be seen that the effect produced by the admixture of salts with sugar, however tested, diminishes as the concentration is diminished, showing that the compound produced in concentrated solutions undergoes decomposition on dilution. Caustic alkalis not only give rise to a larger proportion of "compound" but the product is far less affected by dilution than are those formed from salts.

In whatever way the results are regarded, the facts generally appear to be in accord with the hypothesis that a relatively small proportion of a dissociable compound of sugar and salt is produced—in fact, no other explanation seems to be possible of the values given in the last column of Tables III, IV and V, relating to the influence of concentration, whether of salt or of solvent. Characteristic differences are apparent between the various salts, especially when the sulphates are contrasted with the salts containing monad radicles ; but it is obvious that the relationship of the various substances in solution is of a complex character. The extraordinary influence exercised by sugar on the electrical conductivity of salts in solution is a clear indication, however, that no satisfactory explanation of the phenomena can be given without taking into account the manner in which the solvent is modified by the solute—the need, in fact, of regarding the changes as the outcome of reciprocal interferences.

Table VI.—Effect of non-Electrolytes on the Specific Rotatory Power of Sugar “B.” One gramme-molecule of cane-sugar in 1000 grammes water with addition of 1 gramme-molecule of non-electrolyte.

Non-electrolyte.	Density of solutions.	$[\alpha]_{\text{Hg}}^{25}$		$[\alpha]_{\text{Y}}^{25}$		$[\alpha]_{\text{D}}^{25}$		Dispersion, $[\alpha]_{\text{Hg}} + [\alpha]_{\text{D}}$
		Experiments.	Mean.	Experiments.	Mean.	Experiments.	Mean.	
Acetaldehyde, CH_3CHO	1·10181 1·10176	79·061 79·082	79·07	69·923 69·951	69·94	67·074 67·097	67·09	1·1786
Acetone, $(\text{CH}_3)_2\text{CO}$	1·09301 1·09265	78·350 78·370	78·36	69·327 69·337	69·33	66·494 66·522	66·51	1·1782
Methylic acetate, $\text{CH}_3\text{COOCH}_3$...	1·09948 1·09929	78·351 78·360	78·36	69·316 69·323	69·32	66·457 66·493	66·49	1·1785
Methyl alcohol, CH_3OH	1·09635 1·09650	78·357 78·347	78·35	69·327 69·312	69·32	66·476 66·479	66·48	1·1786
Ethyl alcohol, $\text{C}_2\text{H}_5\text{OH}$	1·09311 1·09309	78·330 78·332	78·33	69·258 69·291	69·27	66·460 66·443	66·45	1·1788
Urea, $\text{CO}(\text{NH}_2)_2$	1·11223 1·11225	78·254 78·246	78·25	69·218 69·211	69·21	66·381 66·386	66·38	1·1788
Pyridine, $\text{C}_5\text{H}_5\text{N}$	1·09806 1·09816	78·228 78·216	78·22	69·168 69·194	69·18	66·338 66·357	66·35	1·1789
Glycerol, $\text{C}_3\text{H}_5(\text{OH})_3$	1·11391 1·11390	78·139 78·146	78·14	69·139 69·158	69·15	66·305 66·311	66·31	1·1784
Chloral hydrate, $\text{CCl}_3\text{CH}(\text{OH})_2$...	1·15193 1·15197	77·682 77·660	77·67	68·739 68·717	68·73	65·934 65·906	65·92	1·1782

Table VII.—Volume Changes in Solutions of non-Electrolytes with and without Cane-sugar. One gramme-molecule of non-electrolyte in 1000 grammes water with or without 1 gramme-molecule of cane-sugar.

Solutes.	Density of solutions.	Total volume of solutions in c.c.	$[V_{Aq+nE} - V_{Aq}]$ in c.c.	$[V_{Aq+nE+Sg} - V_{Aq+Sg}]$ in c.c.
Acetaldehyde	0·99808	1046·04	43·06	
Acetaldehyde + sugar	1·10125	1258·74		43·06
Methylic acetate	0·99873	1075·41	72·43	
Methylic acetate + sugar	1·09950	1288·05		72·37
Acetone	0·98939	1069·39	66·41	
Acetone + sugar	1·09227	1281·93		66·25
Methyl alcohol	0·99124	1041·15	38·17	
Methyl alcohol + sugar	1·09636	1253·41		37·73
Ethyl alcohol	0·98982	1058·19	55·21	
Ethyl alcohol + sugar	1·09328	1271·02		55·34
Urea	1·01210	1047·44	44·46	
Urea + sugar	1·11216	1260·85		45·17
Pyridine	0·99744	1081·85	78·87	
Pyridine + sugar	1·09808	1294·30		78·62
Glycerol	1·01652	1074·31	71·33	
Glycerol + sugar	1·11396	1287·45		71·77
Chloral hydrate	1·06326	1096·06	93·08	
Chloral hydrate + sugar	1·15195	1308·68		93·00

Table VIII.—Effect of Electrolytes on the Specific Rotatory Power of Sugar “A.” One gramme-molecule of cane-sugar in 1000 grammes of water with addition of 1 gramme-molecule of electrolyte.

Electrolyte.	Density of solutions.	$[\alpha]_{\text{Hg}}^{25}$		$[\alpha]_{\text{Y}}^{25}$		$[\alpha]_{\text{D}}^{25}$		Dispersion, $[\alpha]_{\text{Hg}} - [\alpha]_{\text{D}}$.
		Experiments.	Mean.	Experiments.	Mean.	Experiments.	Mean.	
.....	1·10417 1·10416	78·298 78·293	78·30	69·292 69·293	69·29	66·438 66·433	66·44	1·1785
Sodium chloride, NaCl.....	1·13343	77·350	77·35	68·489	68·49	65·654	65·65	1·1782
Potassium chloride, KCl	1·13700 1·13703	77·441 77·445	77·44	68·531 68·541	68·54	65·752 65·743	65·75	1·1778
Lithium chloride, LiCl.....	1·12088 1·12087	77·645 77·640	77·64	68·710 68·693	68·70	65·888 65·889	65·89	1·1783
Ammonium chloride, NH_4Cl	1·11299 1·11301	77·715 77·713	77·71	68·761 68·790	68·77	65·981 65·968	65·97	1·1780
Barium chloride, BaCl_2	1·24075 1·24077	77·724 77·723	77·72	68·757 68·763	68·76	65·939 65·932	65·94	1·1786

Table IX.—Effect of Electrolytes on the Specific Rotatory Power of Sugar “B.” One gramme-molecule of cane-sugar in 1000 grammes of water with addition of one gramme-molecule of electrolyte.

Electrolyte.	Density of solutions.	$[\alpha]_{\text{Hg}}^{25}$		$[\alpha]_{\text{Y}}^{25}$		$[\alpha]_{\text{D}}^{25}$		Dispersion, $[\alpha]_{\text{Hg}} - [\alpha]_{\text{D}}$.
		Experiments.	Mean.	Experiments.	Mean.	Experiments.	Mean.	
.....	1·10403	78·255		69·242		66·388		
.....	1·10404	78·242		69·235		66·399		
.....	1·10403	78·255	78·25	69·242	69·24	66·406	66·40	1·1785
.....	1·10404	78·242		69·235		66·405		
.....	1·10408	78·239		69·233		66·400		
Silver nitrate, AgNO ₃	1·21134	78·080	78·08	69·057	69·06	66·199	66·21	1·1794
	1·21140	78·077		69·053		66·220		
Ammonium nitrate, NH ₄ NO ₃	1·12393	78·067	78·06	69·080	69·07	66·263	66·25	1·1783
	1·12382	78·056		69·067		66·245		
Lithium nitrate, LiNO ₃	1·12444	78·042	78·04	69·056	69·05	66·201	66·21	1·1787
	1·12440	78·045		69·046		66·221		
Calcium nitrate, Ca(NO ₃) ₂	1·16646	78·026	78·03	69·044	69·05	66·226	66·23	1·1782
	1·16651	78·036		69·048		66·224		
Strontium nitrate, Sr(NO ₃) ₂	1·22541	77·855	77·86	68·887	68·89	66·064	66·06	1·1786
	1·22537	77·864		68·895		66·054		
Potassium nitrate, KNO ₃	1·14747	77·813	77·81	68·837	68·83	66·049	66·05	1·1783
	1·14761	77·804		68·829		66·048		
Sodium nitrate, NaNO ₃	1·14388	77·716	77·72	68·745	68·75	65·973	65·98	1·1779
	1·14391	77·720		68·749		65·978		
Barium chloride, BaCl ₂	1·24076	77·692	77·70	68·749	68·75	65·963	65·96	1·1780
	1·24075	77·699		68·756		65·957		
Ammonium chloride, NH ₄ Cl	1·11295	77·669	77·67	68·704	68·70	65·947	65·94	1·1779
	1·11293	77·676		68·703		65·942		
Lithium chloride, LiCl	1·12086	77·623	77·62	68·657	68·66	65·817	65·83	1·1791
	1·12083	77·613		68·665		65·837		
Potassium chloride, KCl	1·13691	77·423	77·42	68·494	68·49	65·684	65·69	1·1786
	1·13699	77·418		68·489		65·691		

Sodium chloride, NaCl	1.13340 1.13339	77.298 77.305	77.30	68.382 68.389	68.39	65.596 65.584	65.59	1.1785
Strontium chloride, SrCl ₂	1.18004 1.18004	77.134 77.127	77.13	68.245 68.245	68.25	65.426 65.420	65.42	1.1790
Potassium bromide, KBr	1.16609 1.16610	77.039 77.037	77.05	68.164 68.169	68.17	65.387 65.368	65.38	1.1785
Calcium chloride, CaCl ₂	1.16415 1.16418	76.952 76.963	76.96	68.069 68.079	68.07	65.278 65.289	65.28	1.1789
Potassium iodide, KI	1.19349	76.067	76.07					
Zinc sulphate, ZnSO ₄	1.22865 1.22866	77.161 77.184	77.17	68.267 68.290	68.28	65.483 65.495	65.49	1.1783
Magnesium sulphate, MgSO ₄	1.19321 1.19321	76.991 76.992	76.99	68.095 68.076	68.09	65.307 65.295	65.30	1.1790
Sodium sulphate, Na ₂ SO ₄	1.19371 1.19369	76.074 76.088	76.08	67.342 67.341	67.34	64.536 64.567	64.55	1.1786
Sodium phosphate, Na ₂ HPO ₄	1.20309	74.590	74.59					
Potassium bicarbonate, KHCO ₃	1.14918 1.15007	77.183 77.166	77.17	68.282 68.284	68.28	65.476 65.474	65.48	1.1785
Potassium carbonate, K ₂ CO ₃	1.18600 1.18615	73.086 73.077	73.08	64.610 64.669	64.64	62.032 62.037	62.03	1.1781
Sodium carbonate, Na ₂ CO ₃	1.18079 1.18081	73.007 73.018	73.01	64.625 64.612	64.62	61.991 61.995	61.99	1.1778
Ammonium hydroxide, NH ₄ OH	1.09486 1.09485	78.006 78.019	78.01	69.005 69.005	69.01	66.198 66.181	66.19	1.1786
Sodium hydroxide, NaOH	1.13548 1.13548	70.651 70.651	70.65	62.524 62.536	62.53	59.915 59.945	59.93	1.1789
Potassium hydroxide, KOH	1.14023 1.14023	70.608 70.590	70.60	62.478 62.472	62.48	59.933 59.927	59.93	1.1780

Table X.—Molecular Conductivity and total Volume of Solutions of Electrolytes with and without Cane-sugar. One gramme-molecule of electrolyte in 1000 grammes of water with or without one gramme-molecule of cane-sugar.

Solutes.	Density of solutions.	Total volume of solutions in c.c.	$[V_{Aq+E} - V_{Aq}]$ in c.c.	$[V_{Aq+E+Sg} - V_{Aq+Sg}]$ in c.c.	Molecular conductivity of electrolyte.
NH ₄ NO ₃	1·02682	1051·90	48·92		100·95
NH ₄ NO ₃ + sugar ...	1·12366	1265·75		50·07	57·603
KNO ₃	1·05531	1043·48	40·50		92·84
KNO ₃ + sugar	1·14761	1257·70		42·02	52·231
NaNO ₃	1·05035	1033·07	30·09		76·32
NaNO ₃ + sugar	1·14409	1247·50		31·82	42·915
LiNO ₃	1·02627	1041·69	38·71		56·580
LiNO ₃ + sugar	1·12416	1255·35		39·67	31·615
AgNO ₃	1·13156	1033·95	30·97		78·50
AgNO ₃ + sugar	1·21129	1248·36		32·68	43·859
Sr(NO ₃) ₂	1·15155	1052·22	49·24		91·52
Sr(NO ₃) ₂ + sugar ...	1·22550	1267·92		52·24	49·990
Ca(NO ₃) ₂	1·08142	1076·44	73·46		88·10
Ca(NO ₃) ₂ + sugar ...	1·16637	1291·39		75·71	48·918
NH ₄ Cl	1·01261	1040·40	37·42		111·73
NH ₄ Cl + sugar	1·11290	1254·09		38·41	63·52
LiCl	1·02045	1021·57	18·59		73·43
LiCl + sugar	1·12072	1235·47		19·79	40·836
KCl	1·04136	1031·92	28·94		112·17
KCl + sugar	1·13704	1246·02		30·34	62·11
NaCl	1·03616	1021·56	18·58		85·91
NaCl + sugar	1·13340	1235·80		20·12	47·610
KBr	1·07703	1039·07	36·09		115·55
KBr + sugar	1·16607	1253·17		37·49	63·45
SrCl ₂	1·09646	1056·58	53·60		119·85
SrCl ₂ + sugar	1·17990	1271·85		56·17	65·29
CaCl ₂	1·07262	1035·78	32·80		123·67
CaCl ₂ + sugar	1·16206	1250·50		34·82	66·07
BaCl ₂	1·16890	1033·71	30·73		138·94
BaCl ₂ + sugar	1·24061	1249·76		34·08	73·41
KI	1·11059	1050·00	47·02		118·34
KI + sugar	1·19349	1263·76		48·08	63·697
Na ₂ SO ₄	1·11254	1026·62	23·64		94·86
Na ₂ SO ₄ + sugar	1·19352	1243·65		27·97	49·899
ZnSO ₄	1·15281	1007·50	4·52		46·776
ZnSO ₄ + sugar	1·22862	1223·83		8·15	22·889
MgSO ₄	1·10972	1009·64	6·66		50·218
MgSO ₄ + sugar	1·19323	1225·73		10·05	24·361
Na ₂ HPO ₄	1·12491	1015·29	12·31		64·06
Na ₂ HPO ₄ + sugar ...	1·20309	1233·71		18·03	31·706
KOH	1·04041	1014·68	11·70		185·57
KOH + sugar	1·13564	1231·30		15·62	45·329
NaOH	1·03873	1001·28	-1·70		151·23
NaOH + sugar	1·13541	1217·37		+1·69	31·046

Table XI.—Alteration in the Rotatory Power of Sugar conditioned by Electrolytes in presence of varying Quantities of Water. One gramme-molecule of cane-sugar and 1 gramme-molecule of electrolyte dissolved in 1000 grammes of water and diluted with 20, 40, 80, 120 or 240 gramme-molecules of water.

Electrolyte.	Additional water.	Density of solutions.	$[\alpha]_{\text{Hg}}^{25}$		$[\alpha]_{\text{Y}}^{25}$		$[\alpha]_{\text{D}}^{25}$		Dispersion, $[\alpha]_{\text{Hg}} \div [\alpha]_{\text{D}}$.
			Experi- mental values.	Mean.	Experi- mental values.	Mean.	Experi- mental values.	Mean.	
Sodium chloride	—	1·13343	77·350	77·35	68·489	68·49	65·654	65·65	1·1782
	20H ₂ O	1·10285	77·609	77·61	68·705	68·71	65·928	65·93	1·1772
	40H ₂ O	1·08414	77·778	77·78	68·830	68·83	66·010	66·01	1·1783
	80H ₂ O	1·06071	77·918	77·92	68·956	68·96	66·203	66·20	1·1778
Potassium hydroxide	120H ₂ O	1·04685	78·051	78·05	69·088	69·09	66·271	66·27	1·1778
	—	1·14023	70·608	70·60	62·478	62·48	59·933	59·93	1·1780
	—	1·14023	70·590	70·59	62·472	62·48	59·927	59·93	1·1780
	40H ₂ O	1·08821	71·382	71·38	63·152	63·15	60·561	60·56	1·1787
Magnesium sulphate	80H ₂ O	1·06401	71·819	71·82	63·500	63·50	60·992	60·99	1·1776
	240H ₂ O	1·02957	73·026	73·03	64·557	64·56	62·041	62·04	1·1771
	—	1·19321	76·991	76·99	68·095	68·09	65·307	65·30	1·1790
	—	1·19321	76·992	76·99	68·076	68·09	65·295	65·30	1·1790
Potassium nitrate	40H ₂ O	{ 1·12274	{ 77·476	77·45	{ 68·557	68·54	{ 65·754	65·74	1·1781
	—	{ 1·12300	{ 77·421	77·45	{ 68·531	68·54	{ 65·729	65·74	1·1781
	80H ₂ O	{ 1·08951	{ 77·693	77·69	{ 68·791	68·80	{ 65·871	65·87	1·1794
	120H ₂ O	{ 1·08952	{ 77·693	77·69	{ 68·804	68·80	{ 65·871	65·87	1·1794
Potassium bromide	—	1·07020	77·824	77·82	68·921	68·92	66·035	66·04	1·1784
	—	1·14747	77·813	77·81	68·837	68·83	66·049	66·05	1·1783
	—	1·14761	77·804	77·81	68·829	68·83	66·048	66·05	1·1783
	40H ₂ O	1·09359	78·081	78·08	68·829	68·83	66·048	66·05	1·1783
Potassium bromide	80H ₂ O	1·06813	78·102	78·10	68·829	68·83	66·048	66·05	1·1783
	120H ₂ O	1·05321	78·193	78·19	68·829	68·83	66·048	66·05	1·1783
	—	1·16609	77·039	77·05	68·164	68·17	65·387	65·38	1·1785
	—	1·16610	77·057	77·05	68·169	68·17	65·368	65·38	1·1785
Potassium bromide	40H ₂ O	1·10508	77·581	77·58	68·164	68·17	65·387	65·38	1·1785
	80H ₂ O	1·07640	77·790	77·79	68·169	68·17	65·387	65·38	1·1785
	120H ₂ O	1·05975	77·947	77·95	68·169	68·17	65·387	65·38	1·1785
	—	1·05975	77·947	77·95	68·169	68·17	65·387	65·38	1·1785

Table XII.—Volume and Conductivity Changes in Mixed Solutions of Sugar and Salts at Various Dilutions. One gramme-molecule of salt dissolved in 1000 grammes of water + 0, 40, 80 or 120 gramme-molecules of water, with and without 1 gramme-molecule of sugar.

Solute.	Extra water.	Density of solutions.	Volume of solutions in c.c.	$[V_{Aq} + E - V_{Aq}]$, in c.c.	$[V_{Aq} + E + Sg - V_{Aq} + Sg]$, in c.c.	$[B - A]$ in c.c.	Molecular conductivity of salt.	Loss in conductivity per cent.
NaCl	—	1·03616	1021·56	18·58	20·12	+1·54	85·91	44·6
NaCl + sugar	—	1·13840	1235·80	18·35	19·23	+0·88	47·61	29·3
NaCl	40H ₂ O	1·02009	1743·47	18·35	19·23	+0·88	91·85	
NaCl + sugar	40H ₂ O	1·08394	1956·44	18·08	18·85	+0·77	64·98	21·6
NaCl	80H ₂ O	1·01345	2465·35	17·95	18·68	+0·73	95·31	
NaCl + sugar	80H ₂ O	1·06066	2678·20	17·95	18·68	+0·73	74·71	17·2
NaCl	120H ₂ O	1·00977	3187·86	6·66	10·05	+3·39	97·97	
NaCl + sugar	120H ₂ O	1·04729	3399·96	4·47	6·76	+2·29	80·74	51·5
MgSO ₄	—	1·10972	1009·64	3·11	4·75	+1·64	50·22	33·9
MgSO ₄ + sugar	—	1·19323	1225·73	2·28	3·99	+1·71	24·36	25·4
MgSO ₄	40H ₂ O	1·06408	1729·59	40·50	42·02	+1·52	63·76	20·7
MgSO ₄ + sugar	40H ₂ O	1·12274	1943·97	39·96	41·00	+1·04	42·13	43·7
MgSO ₄	80H ₂ O	1·04491	2450·38	39·68	40·09	+0·41	71·39	29·2
MgSO ₄ + sugar	80H ₂ O	1·08946	2664·10	39·31	40·09	+0·71	105·11	21·7
MgSO ₄	120H ₂ O	1·03428	3171·69	36·09	37·49	+1·40	82·27	17·1
MgSO ₄ + sugar	120H ₂ O	1·07010	3385·27	35·52	36·00	+0·48	108·07	89·59
KNO ₃	—	1·05531	1043·48	36·09	37·49	+1·40	92·84	45·1
KNO ₃ + sugar	—	1·14761	1257·70	35·67	36·65	+0·98	52·23	30·0
KNO ₃	40H ₂ O	1·03179	1765·08	35·52	36·00	+0·48	100·61	22·3
KNO ₃ + sugar	40H ₂ O	1·09359	1978·21	35·42	35·82	+0·40	71·28	17·6
KNO ₃	80H ₂ O	1·02181	2486·95	3421·30	1039·07	1253·17	105·11	
KNO ₃ + sugar	80H ₂ O	1·06813	2699·44	3421·30	1039·07	1253·17	82·27	
KNO ₃	120H ₂ O	1·01635	3208·72	3421·30	1039·07	1253·17	108·07	
KNO ₃ + sugar	120H ₂ O	1·05321	3421·30	3421·30	1039·07	1253·17	89·59	
KBr	—	1·07703	1039·07	36·09	37·49	+1·40	115·55	45·1
KBr + sugar	—	1·16607	1253·17	35·67	36·65	+0·98	63·45	30·0
KBr	40H ₂ O	1·04448	1760·79	35·52	36·00	+0·48	119·88	22·3
KBr + sugar	40H ₂ O	1·10508	1973·86	35·42	35·82	+0·40	83·88	17·6
KBr	80H ₂ O	1·03074	2482·79	3421·30	1039·07	1253·17	121·90	
KBr + sugar	80H ₂ O	1·07640	2695·35	3421·30	1039·07	1253·17	94·75	
KBr	120H ₂ O	1·02318	3204·82	3421·30	1039·07	1253·17	123·60	
KBr + sugar	120H ₂ O	1·05975	3417·10	3421·30	1039·07	1253·17	101·88	